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Twentieth-Century Chemistry

Edited by Sir William Tilden, F.R.S.
and J. C. Philip, F.R.S.

The Parachor and Valency

The Parachor and Valency

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PREFACE

In the following pages I have endeavoured to give a connected account of the work which has been carried out on the parachor during the last five years. Since the main interest in this constant centres around its contributions to valency theory I have thought it advisable to include a discussion of series spectra, dipole moments, and other physical properties which have played an important part in the development of the modern theory of valency. In this way I have tried to set out clearly the experimental evidence before dealing with the interpretation of valency bonds in terms of electrons.

The development of the electronic theory of valency involves two separate problems which are not always clearly distinguished. The first is concerned with the number of electrons associated with a particular linkage. This problem is now, in my opinion, largely solved, and constitutes the aspect of valency theory which is discussed in the following pages. The second, and much larger problem is that of the stability or reactivity of a molecule. This is obviously determined, not only by the number of electrons in a particular bond, but by the nature of the atoms which are linked by the bond. In many cases the nature and position of other atoms in the molecule have often a large influence upon the stability. On the physical side the first steps have been taken towards a quantitative theory by the wave-mechanics discussion of the structure of H_2^+ and H_2 described in chapter X. From the chemical side the work of Robinson, Ingold, and others is providing a large amount of information as to the relative firmness with which electrons are held; this work, however, is not easily summarised and lies outside the scope of this book.

I have much pleasure in acknowledging the interest and

help of the Editor of this series, Prof. J. C. Philip, O.B.E., D.Sc., F.R.S., at whose suggestion this book was written. I am also indebted to my colleagues, Dr. W. W. Myddleton and Dr. H. Nettleton, who have been good enough to read the proofs.

S. S.

LONDON,
August, 1929.

CONTENTS

CHAPTER		PAGE
I.	The Liquid State	1
II.	Empirical Relations between Surface Tension, Density, and Temperature	23
III.	The Parachors of Organic Compounds	33
IV.	Atoms and Spectra	53
V.	Polar and Non-Polar Linkages	84
VI.	Higher Valencies	114
VII.	Applications of the Theory of Odd Electron Linkages	138
VIII.	Associated Liquids	157
IX.	Atomic Parachors and Atomic Number	181
X.	The Quantum Theory of Shared Electrons	191
XI.	Experimental Methods	203
	Index	223

THE PARACHOR & VALENCY

CHAPTER I

THE LIQUID STATE

General Properties of Liquids

THE most striking feature of the transition from the gaseous to the liquid state is the very large decrease in volume which accompanies this change. A familiar example is the condensation of steam at 100°, in which roughly 1600 c.c. of steam at normal pressure are required to produce 1 c.c. of liquid water. From the standpoint of molecular theory it follows that the characteristic difference between gases and liquids is the very different distribution of their molecules in space. The properties of gases are largely determined by the fact that the molecules are separated by distances which are large compared with their diameter; for this reason gases exhibit regularities in behaviour which are not found for liquids or solids. Thus the pressure, volume, and temperature relationships which are summarised in the gas laws are dependent almost entirely upon the number of molecules present in unit volume, and are influenced only to a minor extent by the nature of the molecules and the forces which they exert upon one another. In the liquid state, on the other hand, we have to deal with an assemblage of molecules separated by much smaller distances.

This is very clearly indicated by the results of modern measurements of the dimensions of molecules. The viscosity of a gas can be shown to depend upon the diameter of the molecule and according to the elaborate mathematical investigation of Chapman* is given by

$$\sigma^2 = \frac{0{\cdot}499\, m \bar{c}}{\sqrt{2}\,\pi\,\eta} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

* *Phil. Trans.*, 1915, A **216**, 279.

Here σ is the diameter of the molecule, supposed to be spherical, m is its mass, and $\bar{c}$ its average velocity, whilst η is the viscosity. If this formula is applied to measurements of the viscosity over a range of temperature, it is found that the values of σ decrease as the temperature rises and tend to a limiting value at high temperatures. This behaviour is ascribed, not to any actual change in the volume of the molecule, but to the effect of the fields of force which surround it. According to Chapman the picture of a molecule which best fits the facts is that of a rigid core surrounded by a weak attractive field of force. This model when analysed mathematically leads to a formula proposed much earlier by Sutherland,* namely

$$\sigma^2 = \sigma_\infty{}^2\left(1 + \frac{C}{T}\right) \qquad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where C is known as Sutherland's constant and T the absolute temperature. For most gases this expression gives a constant value for σ_∞, which may be taken as the diameter of the rigid core and gives us the most reliable value for the diameter of a molecule which is available at the present time.

We can use the diameters obtained in this manner to discuss the distribution of molecules in the liquid state; this is best done in the following manner. Let V represent the volume of one gram-molecule of a liquid under some given conditions; if the liquid is regarded as an assemblage of spheres of diameter s packed as closely as possible, then

$$V = \frac{Ns^3}{\sqrt{2}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Here N is Avogadro's number ($6{\cdot}062 \times 10^{23}$), and s may be interpreted as the average distance between the centres of adjacent molecules in the liquid. By comparing the values of s obtained under different conditions with the value of σ from gas viscosities, we can judge how closely molecules approach one another in the liquid state.

Data of this kind for a number of liquids are given in table 1. Too much stress must not be laid upon the actual figures, since the assumption of spherical molecules is probably not accurate, particularly for the more complex molecules. It is evident, however, that a liquid must be regarded as a very

* *Phil. Mag.*, 1893 [5], **36**, 507.

coarse-grained structure; at the boiling point the average distance between the centres of adjacent molecules is usually less than one and a half times the molecular diameter, so that the distance between the edges of adjacent molecules must be less than half their diameter. Even at the limit of the liquid state, the critical temperature, the distance between the edges of adjacent molecules is barely one diameter. It will be noted that hydrogen and helium are anomalous, particularly at the boiling point. This is probably due to the large repulsive forces between their molecules at very small distances. These two gases are peculiar in their electronic constitution, since

TABLE I

Molecular Dimensions and the Liquid State

Substance.	*Molecular volume at*		*Mean distance between molecules at*		
	b.p.	*crit. temp.*	*b.p.*	*crit. temp.*	σ_∞
Hydrogen	28·7 c.c.	46·9 c.c.	$4{\cdot}06 \times 10^{-8}$cm.	$4{\cdot}78 \times 10^{-8}$cm.	$2{\cdot}42 \times 10^{-8}$cm.
Helium . .	31·9	57·7	4·21	5·12	1·94
Neon . .	16·8	41·7	3·40	4·60	2·32
Argon . .	28·5	75·3	4·05	5·60	2·90
Krypton . .	34·3	92·0	4·31	5·99	3·13
Xenon . .	42·5	112·7	4·63	6·40	3·44
Ammonia. .	25·2	71·9	3·87	5·51	3·14
Methane . .	—	98·6	—	6·13	3·12
Benzene . .	95·7	256·1	6·07	8·42	4·20
Ethyl acetate .	106·2	286·0	6·28	8·74	4·37
Propyl acetate .	127·6	345·3	6·68	9·30	4·67

The data for the inert gases are taken from Abegg's *Handbuch der anorganischen Chemie*, Vol. IV, 3rd. Abt., 1st Teil, p. 359, and those for the other gases from Landolt-Börnstein-Roth's tables.

they do not contain the complete octet of electrons which in most cases screens the positively charged nuclei and reduces the repulsive forces between two molecules. It is interesting to note that gaseous helium can be compressed at a pressure of 15,000 kilogram/cm.^{2} to a density three times as great as that of the liquid; under these conditions the mean distance between the molecules becomes $3{\cdot}0 \times 10^{-8}$ cm.

The coarse-grained structure of liquids is not alone sufficient to account for their characteristic properties, for in solids and in highly compressed gases above the critical temperature, the same close approach of the molecules is found. It is necessary to consider also the effect of the kinetic energy of the molecules which limits the range of existence of the liquid

state in two directions. If the translational energy falls below a certain critical value, practically all the molecules become fixed in a definite space lattice and the liquid crystallises. On the other hand, as the temperature is raised, another limiting value of the kinetic energy is reached at the critical temperature, which is the upper limit of existence of the liquid state. The properties of liquids are therefore conditioned by three sets of forces: (a) the external pressure, (b) the forces exerted by the molecules upon each other, and (c) the thermal forces due to the motion of the molecules. At the distances at which molecules are found in liquids, the net effect of the action of molecules upon each other is undoubtedly such as to produce a force of attraction between them; this tends to compress the liquid and thus gives rise to an internal pressure acting in the same direction as the external pressure. This pressure is termed the *cohesion*, and is defined in the following manner. Imagine any plane within the liquid, the cohesion is the force exerted per unit area across this plane by the attraction of the liquid on one side for that on the other. The cohesion and external pressure are balanced by the forces due to molecular agitation which are sometimes described as the thermal pressure, or more commonly as the intrinsic pressure of the liquid. We have thus an equilibrium given by

External Pressure + Cohesion = Intrinsic Pressure.

We are still ignorant of the quantitative laws which govern cohesion and intrinsic pressure in the liquid state, for the forces which molecules exert upon one another at small distances cannot be represented by any simple formula. For gases above the critical temperature an approximate representation of this equilibrium is given by the well-known equation of van der Waals when this is written

$$P + \frac{a}{V^2} = \frac{RT}{V-b} \quad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Here a/V^2 represents the cohesion and $RT/(V-b)$ the intrinsic pressure. This equation cannot of course be applied to liquids with any accuracy, since the expressions for cohesion and intrinsic pressure are then much more complex.

If we are considering liquids at moderate external pressures then this pressure can often be neglected, since it is small compared with the large values of several thousands of atmospheres found for the cohesion. Under these conditions

the cohesion and the intrinsic pressure have nearly the same numerical value, though they are opposite in sign.

Surface Tension and Contact Angle

The mutual attraction of the molecules gives rise to another effect at the surface of a liquid, for the molecules in the surface layer are subjected to a one-sided attraction which tends to draw them below the surface. A liquid surface therefore possesses special properties which are usually classified under the heading of "*capillary action.*"

When a capillary tube, i.e. a tube as fine as a hair, is dipped into water the liquid rises in the tube and ultimately comes to rest at a higher level than the bulk of the water. If, instead of water, mercury is used, the liquid level within the tube is found to be depressed. The action between the tube and the liquid in these cases was first termed "capillary action," but this expression is now extended to cover a large number of other phenomena which depend upon the properties of liquid surfaces.

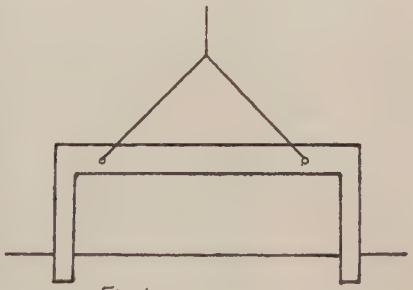


Fig. 1

The rise of liquids in capillary tubes was first studied by Leonardo da Vinci in the seventeenth century, but it was not until 1751 that J. A. von Segner* introduced the important conception of surface tension which may be defined as follows. The surface of a liquid tends to contract and is therefore under tension ; this tension, measured across any line drawn on the surface of the liquid, is normal to that line and is the same at every point and in every direction on the liquid surface. It is also practically independent of the curvature of the surface ; if, however, the radius of curvature is so small that it approaches the molecular diameter, the mathematical theories of surface tension in terms of molecular attractions indicate that the tension of a concave surface becomes greater than the

* *Comment. Soc. Reg. Götting.*, 1751 (i), 301.

normal value whilst that of a convex surface is less. This effect is, however, negligibly small for the most sharply curved surfaces which can be realised experimentally.

The tension of a liquid surface can be illustrated and measured approximately by means of a simple experiment due to Dupré. A light metal frame of the shape in fig. 1 is suspended from a balance with the lower end dipping into soap solution. The frame is first dipped completely into the solution, and is then lifted to form a rectangular film as shown in the figure. After a few minutes, when excess of liquid has drained away, the balance is brought into adjustment by adding suitable weights ; the film is then punctured by touching it with a hot needle and the balance readjusted. It will be found that the frame appears to weigh less after the film has been destroyed, since the tension of the film is no longer pulling it towards the liquid surface. In this experiment two surfaces of the film are in action and must be allowed for in calculating its tension.

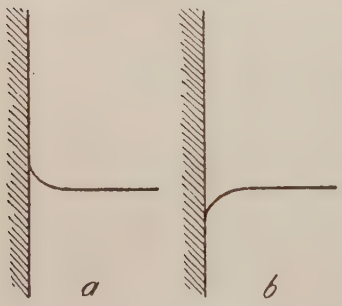


Fig. 2

The behaviour of a liquid in contact with a solid depends upon the properties of the solid as well as upon the surface tension of the liquid. Thus water, in contact with clean glass, gives a surface of the type shown in fig. 2a with the glass a tangent to the water-air surface. For mercury and glass the surface takes the form shown in fig. 2b in which the air-mercury surface meets the glass at an angle of about 140°. There is a definite contact angle for each pair of fluids in contact with a solid which can have any value from 0° to 180°. For water, and most organic liquids, in contact with clean glass this angle is zero, but with greasy glass water gives a large angle. Systems in which two fluids are in contact with a solid, e.g. water-chlorobenzene-glass, often show contact angles approaching 90°.

The magnitude of the contact angle depends upon an equilibrium between (a) the mutual attraction of the molecules of the liquid, and (b) the attraction of the solid for the liquid. If the latter is much greater than the mutual attraction of the

liquid molecules the liquid tends to spread over the solid and the contact angle is small; if, however, the mutual attraction of the liquid molecules is greater than the attraction of the solid for the liquid, the latter does not " wet " the solid and the contact angle is large.

The first correct theory of the rise of liquids in capillary tubes was given in 1802 by Leslie.* He supposed that the material of the tube attracted the molecules of the liquid by a force which is everywhere normal to the solid; the direct effect of this attraction is to increase the pressure on the layer of fluid in contact with the solid and thus cause it to spread over the surface. The liquid at the periphery rises and carries with it by cohesion a column of liquid until the weight of this column is balanced by the capillary forces at the periphery.

The mathematical treatment of the forces between molecules is found to be very complex, and we are still ignorant of the laws which govern intermolecular attractions. The form of a liquid surface under given conditions can, however, be determined from its surface tension and contact angle *without further analysis in terms of molecular forces.* The fundamental equation was given by Laplace, who showed that, for any law of force between molecules which makes the attraction become negligibly small at distances greater than a few molecular diameters, there is a definite relation between the curvature of a surface, its surface tension, and the pressure difference between the two sides of the surface. This relation is defined by the equation

$$p = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

where γ is the surface tension, p the pressure difference, and R_1 and R_2 are the principal radii of curvature of the surface. For a plane surface the radii of curvature become infinite and the pressure is the same on both sides. A plane surface is therefore used from which to measure capillary rise, etc., or else, if the vessel used to hold the liquid is not of sufficient size to give a surface with practically no curvature, a suitable correction has to be applied.

A simple application of this equation gives the pressure inside a small bubble of gas in a liquid. If the bubble is small it may be supposed to be a sphere and the radii of curvature

* *Phil. Mag.*, 1802, **14**, 193.

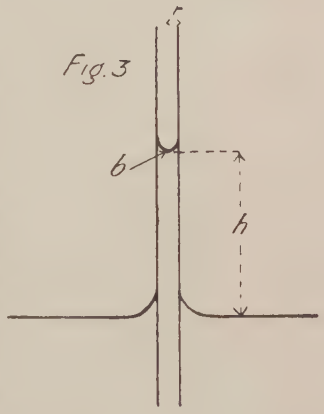
at all points will be equal to the radius of the bubble r. The pressure within the bubble will then exceed the pressure in the liquid just outside the bubble by $2\gamma/r$. If r is very small this excess of pressure can become very large. Thus, for a bubble of radius 10^{-5} cm. in water, which has a surface tension of about 70 dynes/cm., the extra pressure within the bubble is about 14 atmospheres. This effect of surface tension on bubble pressure is responsible for the superheating and "bumping" of liquids in the neighbourhood of their boiling points. If the liquid is quite free from gas bubbles then the vapour pressure of the liquid is not sufficient to start a bubble, or even to make a very small bubble grow, until the temperature rises well above the boiling point; once a bubble is started any increase in its size lowers the pressure effect due to surface tension, so the bubble grows very rapidly, giving sudden and violent boiling of the liquid. The addition of porous pot provides nuclei of air bubbles of such a size that the excess pressure due to surface tension is small; the vapour pressure of the liquid at the boiling point is then sufficient to expand these bubbles and the liquid boils quietly.

Methods of Measuring Surface Tension

Since Laplace's equation applies generally to any liquid surface it can be made the basis of a large number of methods of determining surface tension, for this quantity is known when the curvature of the surface and the pressure difference at any point have been determined. The curvature of drops and bubbles, the adhesion of plates and rings to a liquid surface, the rise of liquids in capillary tubes, the pressure required to form bubbles from a capillary tube, the weight of falling drops and the formation of ripples on liquid surfaces have all been used for this purpose. These many and varied methods are of interest from the standpoint of physics, for they provide a thorough test of the hypothesis of constant surface tension over a wide range of experimental conditions. For physico-chemical investigations, however, many of these methods are unsuitable. The chemist requires a method which is applicable to as large a range of substances as possible; many of the compounds he wishes to examine are difficult to obtain in quantity or are highly reactive, so that he must abandon those methods which require large volumes of liquid or expose large surfaces to the atmosphere. Because of these limitations only

three of the many methods of measuring surface tension have found wide application in physical chemistry, namely, those based upon observations of capillary rise, bubble pressure, and the weight of falling drops.

The elementary theory of the method of capillary rise is easily deduced from the fundamental equation of Laplace (5). Let us suppose that a capillary tube of radius r is dipped into a vessel of sufficient size to give a plane surface to the liquid it contains. Let the height to which the liquid rises inside the tube measured from this plane surface be h (fig. 3). If the tube is vertical the meniscus will be a figure of revolution and the radii of curvature at the lowest point will be equal and have some value b. From Laplace's equation it follows that the pressure at a point in the liquid just below the meniscus will be less than atmospheric pressure by $2\gamma/b$. The pressure below the plane surface is, however, equal to the atmospheric pressure, and the difference in pressure between these two points must be equal to the hydrostatic pressure of the liquid in the tube. Equating these two values for the pressure difference we have



$$\frac{2\gamma}{b} = hgD \text{ or } \gamma = \tfrac{1}{2}hgDb \quad \ldots\ldots\ldots\ldots\ldots\ldots (6)$$

where D is the density of the liquid and g the gravitational constant.

This equation is exact but contains the unknown quantity b. If the tube is very small and the contact angle is zero, then the meniscus is very nearly a hemisphere, so that $b = r$ and

$$\gamma = \tfrac{1}{2}hgDr \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

For larger tubes it is necessary to use Laplace's equation to investigate the form of the meniscus and obtain an expression connecting r and b. This question is discussed in detail in a later chapter (p. 215).

The measurement of surface tension by means of capillary

rise has many practical advantages. The capillary and liquid can be sealed up in a strong glass vessel and measurements made up to the critical temperature, as in the classical work of Ramsay and Shields. For the same reason it is peculiarly valuable in dealing with reactive and hygroscopic substances. Its disadvantages are twofold. The surface of the liquid within the tube is small and is not easily renewed; any impurities tend to collect at such a surface and usually lower the surface tension. Great care has therefore to be taken in cleaning and drying the apparatus. The second difficulty lies in the fact that the capillary rise depends upon the contact angle as well as upon the surface tension, and for a small tube with a liquid of contact angle θ the equation should be written

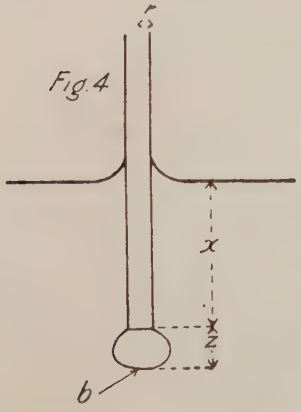


Fig. 4

$$\gamma \cos\theta = \tfrac{1}{2}hgDr \quad \ldots\ldots\ldots\ldots\ldots (8)$$

Thus, a contact angle of 8° introduces an error of one per cent in the value found for the surface tension. Fortunately most organic substances have contact angles with clean glass which are zero or very nearly zero, so that $\cos\theta$ can be taken as unity.

The method of maximum bubble pressure is based upon observations of the pressures required to liberate bubbles from a capillary tube immersed vertically in a liquid (fig. 4). Let a tube of radius r be immersed to a depth x below a plane liquid surface, and a slowly increasing pressure be applied to the gas within the tube. If we consider the conditions at the lowest point of the bubble which commences to grow at the end of the tube, then the pressure within the bubble will, by Laplace's equation, exceed the pressure outside by $2\gamma/b$, where b is the radius of curvature at the vertex. If the depth of the vertex of the bubble below the tube is z, then to this excess must be added the hydrostatic pressure at this point so that the pressure within the bubble is given by

$$p = \frac{2\gamma}{b} + gD(x + z) \quad \ldots\ldots\ldots\ldots\ldots (9)$$

Here p is the difference between the pressure in the bubble and

that of the atmosphere above the plane surface of the liquid. As the bubble increases in size b increases, and the first term of this expression diminishes ; at the same time the depth of the bubble, z, is increasing so that the second term is increasing. These opposing tendencies cause the pressure to rise to a maximum value and then diminish as the bubble increases in size. (In practice the bubble grows slowly until the maximum pressure is reached, and then, since a supply of gas at the maximum pressure is available, the bubble rapidly increases in size and breaks away from the end of the tube. The maximum pressure can therefore be approached at a sufficiently slow rate to permit of accurate observation, and the subsequent behaviour of the bubble has no influence on the results.)

For very small tubes it can be shown that the maximum pressure is reached when the bubble is a hemisphere ; under these conditions $b = r$ and $z = r$, so that

$$p_{\max.} = \frac{2\gamma}{r} + gD(x + r)$$

$$\gamma = \frac{r}{2}\left[p_{\max.} - gD(x + r)\right] \ldots\ldots\ldots (10)$$

With larger tubes this simple formula no longer holds, for the bubble passes the stage corresponding to a hemisphere before the maximum pressure is reached. It is necessary to use Laplace's equation to deduce the shape of the bubble and the point at which the maximum pressure is reached. This question is discussed in detail in Chapter XI (p. 217).

This method has many advantages when the substance can be studied at atmospheric pressure. Since a new surface is formed by each bubble, traces of impurities adhering to the capillary are soon carried away and do not influence the results. The method can also be used over a wide range of temperatures, since the capillary and containing vessel can be placed in a suitable furnace or cryostat and connected to a separate manometer outside, on which the maximum pressure can be read with accuracy. The surface tensions obtained by this method are not dependent upon the contact angle, since this does not fix the maximum pressure.

The third method depends upon observations of the weight

of a drop of a liquid which falls from a tip of known diameter. When a drop is made to grow slowly as it hangs from the end of a vertical tube it is found to assume successively the shapes shown in fig. 5. These stages can easily be demonstrated by forming drops of aniline in a solution of slightly lower density ; under these conditions large drops are formed which settle slowly when they break away from the tube so that the process by which the drop is detached can readily be followed. Drops of liquids falling in air have also been investigated by stroboscopic methods and by the cinematograph camera, and are found to behave in a similar manner. The stages *a*, *b*, and *c* are controllable and the drop can be maintained indefinitely in these states by stopping the flow of liquid. At *d*, a critical stage is reached when a constriction appears ; this rapidly

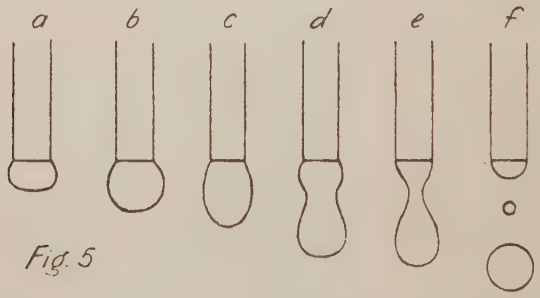


Fig. 5

develops until the lower part of the drop breaks away, usually accompanied by one or more very small drops formed in the later stages of detachment at the narrowest part of the neck. The changes from *d* to *f* take place very quickly and cannot be controlled ; once the drop has passed the critical stage the separation of the lower portion cannot be prevented by withdrawing liquid.

A partial mathematical treatment of the equilibrium of pendent drops has been given by Bashforth and Adams and has been extended by Lohnstein, and others. These discussions are essentially statical and apply only to the equilibrium conditions : the factors which determine what proportion of the drop falls away must obviously depend upon the dynamics of the drop in the later stages. A dynamical discussion would be very complex and does not seem to have been attempted. The problem can, however, be attacked experimentally by

investigating the weight or volume of drops of a liquid of known surface tension which fall from a tip of known diameter. It was supposed by many of the earlier workers on this subject that, for a given tip, the weight of a drop was proportional to the surface tension; this is only approximately true for liquids whose surface tensions and densities bear a definite relation to the tip diameter. The most accurate experimental determination of the relation between drop weight and surface tension is that of Harkins and Brown,* who found that the surface tension is given by

$$wg = 2\pi r\gamma\phi' \quad \ldots\ldots\ldots\ldots\ldots\ldots (11)$$

Here w is the apparent† weight of the drop, g the gravitational constant which can be taken as 981, r the radius of the tube, and ϕ' a correction factor which is found to be determined solely by the ratio $r/v^{\frac{1}{3}}$, where v is the volume of the drop. Values of this factor can be tabulated for a range of values of r/v, and provided that the data for a range of liquids and tips all lie on a smooth curve these values can be used to calculate surface tensions from drop weights. It is convenient to rearrange the equation of Harkins to include the numerical constants in the factor. Writing

$$\gamma = \frac{g}{2\pi\phi'} \cdot \frac{w}{r} = \phi w/r \quad \ldots\ldots\ldots\ldots\ldots\ldots (12)$$

the standard values of ϕ can be obtained from observations of w and r for liquids of known surface tension.‡ The data in table 2 show the constancy of ϕ for liquids of different surface tension when the ratio $r/v^{\frac{1}{3}}$ is the same.

* *J. Amer. Chem. Soc.*, 1919, **41**, 499.

† Strictly $w = W_v(D - d)/D$, where W_v is the weight of the drop in vacuo, D the density of the liquid, and d the density of the surrounding medium (e.g. air + vapour). When the drop method is used to measure interfacial tensions d becomes large; for non-volatile liquids of density about 1·0 falling in air the error introduced by taking w as the weight in air (as usually determined with brass weights) is less than 0·1%.

‡ This equation neglects the variation of g with latitude and height above sea-level. The necessary correction is readily introduced; except in tropical latitudes and at high altitudes the error caused by taking g as constant is less than 0·1%, and few surface tensions are known with this accuracy.

TABLE 2

Drop Weights and Surface Tension

Substance	r	w	$r/v^{\frac{1}{3}}$	ϕ
Benzene . .	0·19724	0·022413	0·6701	254·2
Water . .	0·29423	0·08427	0·6705	254·1
Benzene . .	0·24456	0·027204	0·7789	259·6
Water . .	0·37964	0·10623	0·8008	260·1
Benzene . .	0·29694	0·032938	0·8873	260·4
Water . .	0·44755	0·12522	0·8937	260·3
Benzene . .	0·34188	0·038320	0·9713	257·7
Water . .	0·50087	0·14142	0·9604	257·8

A long series of such observations have been made by Harkins and Brown using liquids with widely different densities, viscosities, and surface tensions. The values of ϕ calculated from these observations are all found to lie on a smooth curve when plotted against $r/v^{\frac{1}{3}}$. The average values of ϕ read from this curve are tabulated below and are probably accurate to 1 part in 1000. For the values of $r/v^{\frac{1}{3}}$ ranging from 0·60 to 1·00

TABLE 3

Drop-weight Correction Factors

$r/v^{\frac{1}{3}}$	0·00	0·01	0·02	0·03	0·04	0·05	0·06	0·07	0·08	0·09
0·30	215·0	216·3	217·6	218·9	220·2	221·5	222·8	224·1	225·4	226·7
0·40	228·0	229·3	230·6	231·9	233·2	234·4	235·6	236·7	237·8	238·9
0·50	240·0	241·0	242·0	243·0	244·0	245·0	245·9	246·8	247·7	248·6
0·60	249·5	250·3	251·0	251·7	252·4	253·0	253·6	254·2	254·8	255·4
0·70	255·9	256·4	256·9	257·4	257·9	258·3	258·7	259·1	259·4	259·7
0·80	260·0	260·2	260·4	260·5	260·5	260·5	260·5	260·5	260·4	260·3
0·90	260·1	259·8	259·5	259·2	258·9	258·6	258·2	257·8	257·2	256·6
1·00	256·0	255·3	254·5	253·7	252·8	251·9	251·0	250·1	249·3	248·5
1·10	247·6	246·8	245·9	245·0	244·2	243·3	242·5	241·7	240·9	240·1

ϕ varies only slowly and has been well determined so that it is preferable to select tips of such a diameter that the drops will come into this range. The use of table 3 in calculating surface tensions from drop weights will be obvious from the following example. Harkins found that at 20° a tip of 0·3419 cm. radius gave a drop of water weighing 0·09639 gm. The

volume of the drop was 0·09675 c.c., so that $r/v^{\frac{1}{3}} = 0{\cdot}7450$. From the table this corresponds to $\phi = 258{\cdot}1$, whence $\gamma = w\phi/r = (0{\cdot}9639 \times 258{\cdot}1)/0{\cdot}3419 = 72{\cdot}75$ dynes/cm., in good agreement with the standard figure 72·80.

Iredale* has criticised the formula used by Harkins and his co-workers and suggests a return to an equation given earlier by Worthington,† namely

$$\frac{\gamma_1/\rho_1}{\gamma_2/\rho_2} = K^2 = \frac{r_1^2}{r_2^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots (12)$$

Here γ_1 and γ_2 are the surface tensions of two liquids of densities ρ_1 and ρ_2; r_1 and r_2 are the radii of two tips from which the liquids give drops of radii r'_1 and r'_2 (the drops are treated as spheres), which are chosen by the condition that $r_1/r'_1 = r_2/r'_2$. By tabulating values of the ratio r/r' against r for a given liquid, this equation can be used to calculate surface tensions from drop weights, but the calculation is rather involved and confusing. Moreover, the equations of Harkins and Worthington are really identical,‡ for one can be deduced from the other without introducing any approximations. Thus, from Harkins' equation

$$\frac{\gamma}{\rho} = \frac{w}{\rho} \cdot \frac{\phi}{r} = \frac{v\phi}{r}$$

Hence for two liquids

$$\frac{\gamma_1\rho_1}{\gamma_2\rho_2} = \frac{v_1}{v_2} \cdot \frac{r_2}{r_1} \cdot \frac{\phi_1}{\phi_2}$$

and if $r_1/r_1' = r_2/r_2''$, then $\phi_1 = \phi_2$ and $\frac{v_1}{v_2} = \left(\frac{r_1'}{r_2'}\right)^3 = \frac{r_1^3}{r_2^3}$

Hence $\frac{\gamma_1/\rho_1}{\gamma_2/\rho_2} = \frac{r_1^2}{r_2^2}$, which is Worthington's formula.

For accurate work it is necessary to ensure that the drops are formed slowly and that premature disruption is not brought about by vibration. Either drop weights or drop volumes may be measured; the latter method has certain advantages when working with volatile liquids and also in the measurement of interfacial tensions. The surface tensions found by the drop method do not appear to be influenced by the contact angle, so that this method is applicable to the study of liquids such as mercury and other fused metals.

* *Phil. Mag.*, 1923, **45**, 1088.
† *Ibid.*, 1899 [5], **48**, 321.
‡ Assuming g is constant, cf. p. 13.

Magnitude of the Cohesion

The cohesion of a liquid cannot be measured directly, and to gain some idea of its value it is necessary to use approximate formulæ which connect some other property of the liquid with this internal pressure. These formulæ are obtained either by thermodynamical reasoning in which important approximations are made, or else by the use of a particular hypothesis with regard to the law of force between molecules. The absolute value of the cohesion obtained by these methods cannot therefore be regarded as accurate, but the figures obtained serve to indicate the order of magnitude of the cohesion and the manner in which it varies with temperature.

A relation between the coefficient of expansion, α, the compressibility, β, and the intrinsic pressure, π, of a liquid (which can be taken as equal to the cohesion) was obtained by Dupré* of the form

$$\pi = -T\frac{\alpha}{\beta} \quad \ldots\ldots\ldots\ldots\ldots\ldots (13)$$

Some values of the cohesion calculated by this equation are given in table 4. The approximate nature of this formula will be realised when the behaviour of water at 4° is considered. At this temperature α for water changes sign whilst β does not ; hence a strict application of Dupré's equation would lead to the absurd conclusion that the intrinsic pressure of water below 4° is negative.

The cohesion is obviously related to the latent heat of evaporation of a liquid, for the work required to carry a molecule from the surface of a liquid to an infinite distance is determined by the forces of attraction between the molecules. Dupré (loc. cit.), and later Edser,† from a particular hypothesis as to the law of attraction conclude that the cohesion is equal to the internal latent heat per unit volume or that

$$K = \lambda D \quad \ldots\ldots\ldots\ldots\ldots\ldots (14)$$

where λ is the internal latent heat per gram and D the density. Some figures obtained by the use of this formula are quoted in table 4.

Surface tension and cohesion are both produced by molecular attractions, but the relation between them depends upon

* *Ann. Chim. Phys.*, 1864, **2**, 201.

† *Fourth Report on Colloid Chemistry*, H.M. Stationery Office, 1922, p. 67.

the law of attraction between molecules which is still not completely understood. If we accept the hypothesis of Edser (loc. cit.) the relation between these quantities is given by

$$K = \frac{4\gamma}{\delta} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (15)$$

where δ is the diameter of the molecule. Some values of the cohesion calculated in this way are given in table 4. The molecular diameter can be obtained from the density of the densest form of the substance, from van der Waals' b, and in other ways, but is not certain to within 10%.

TABLE 4

Cohesion of Liquids

	Cohesion in megabars calculated from					
	Compressibility.		*Latent Heat.*		*Surface Tension.*	
Octane .	20°	2970	120°	1840	20°	1460
CCl_4 . .	20°	3690	100°	2640	20°	2030
$CHCl_3$.	20°	3880	60°	3620	20°	2170
Benzene .	20°	4100	70°	3330	20°	2230
Bromine .	20°	5400	58°	5700	20°	3020
Mercury .	20°	13200	357°	36100	20°	60600

(For a discussion of other methods of obtaining approximate values of the internal pressure, see Hildebrand, *Solubility*, Chem. Catalogue Co., New York.)

It is evident from the figures in this table that these methods of calculation can only be taken as giving rough values of the cohesion and must be regarded as indicating the order of magnitude of the internal pressure rather than its absolute value. It follows that this pressure amounts to several thousands of atmospheres (1 megabar = 0·987 atm.) and shows a large variation from liquid to liquid. Since latent heats and surface tension decrease with rising temperature, the cohesion also diminishes rapidly as the temperature rises and becomes very small at the critical temperature.

Forces between Molecules

When the molecules of a vapour are brought together by compression it is evident that they exert forces of attraction upon one another which produce, first, deviations from the gas laws, and ultimately liquefaction, accompanied by a large

diminution in volume. There is a considerable amount of evidence to show that these attractive forces fall off very rapidly with distance and become inappreciable at distances greater than a few molecular diameters. Thus the surface tension of a soap film remains constant until a thickness of about 10^{-6} cms. is reached, and the effect of films of oil upon the surface tension of water becomes constant at about the same thickness, so that this number represents an upper limit for the effective range of the molecular forces.

The modern electronic theories of atomic structure compel us to picture the molecule as an assemblage of electrons grouped around a positive nucleus. It is readily shown that such a model gives, for a neutral molecule, no resultant forces either of attraction or repulsion at distances which are large compared with the molecular diameter. When two such molecules approach one another the forces between them will depend upon the relative configurations of the electrons and nuclei at the moment of approach. With a chance distribution it would seem at first sight that the probability of a configuration giving a force of attraction is exactly the same as that for a configuration which produces repulsion, so that the average effect would be zero. When, however, the problem is investigated more closely by statistical methods* it is found that there should be a net attractive force which arises in the following manner. When two molecules approach one another in such a way that the force between them is one of attraction, then this force causes the two molecules to remain close to one another for a rather longer time than usual ; in the contrasting case in which the disposition of the electrons and nuclei produce a force of repulsion, the time occupied by the collision is shortened. Thus the duration of collisions in which the molecules are so disposed as to produce attractive forces is greater, and on the average an attraction between the molecules should be found. In this way one can account for the fact that even the inert gases, whose molecules must on many grounds be regarded as possessing a very small external field, can be liquefied and solidified.

It is evident from the fact that the encounter between two molecules is an elastic collision that, as the distance between the molecules is made very small, the force of attraction must

* Cf. Jeans, *J.C.S.*, 1923, **123**, 3408.

change at a certain point into one of repulsion. Some information about this force can be obtained from the study of the viscosities of gases, from which the mean collision area of the molecule can be calculated. This represents the average area marked out around a particular molecule by the points of closest approach of colliding molecules. As the temperature rises this area diminishes slowly, since the molecules have a higher velocity and can penetrate further against the repulsive forces. From the manner in which the collision area varies with temperature, it is found that the repulsive force varies inversely as a high power of the distance. For instance, Jeans (loc. cit.) suggests forces ranging from the inverse 12th power for very "hard" molecules to the inverse 5th power for "softer" molecules. Similar conclusions can be drawn from the compressibility relations of liquids and from the study of crystals. In the latter case considerable success has been attained in predicting the properties of crystals on the assumption that the forces between the ions in the crystal lattice can be expressed by an equation of the type

$$f = \frac{\alpha}{r^m} - \frac{\beta}{r^n} \quad \ldots\ldots\ldots\ldots\ldots\ldots (16)$$

where f is the force between two molecules separated by a distance r, and α, β, m, and n are constants. It is evident on general grounds, therefore, that the forces between molecules in the liquid state can probably not be represented by any simple formula, and that both the attractive and repulsive forces must be taken into account.

Theories of Molecular Attraction

The mathematical theory of capillary action was first developed by Young* and by Laplace,† and has been extended and corrected by Gauss, Poisson, and other later workers.‡ The object of these theories is to describe the behaviour of liquids in terms of the forces between the molecules and to ascertain the laws which govern the variation of this force with the distance between the molecules.

In the first place, it has been shown that, provided the

* *Phil. Trans.*, 1805, p. 65.
† *Mécanique céleste*, supplement to the 10th book, 1806.
‡ For a useful summary of the fundamental equations, see Rayleigh, "Capillary Action," *Encyclopædia Britannica*, 11th Ed.

force between the molecules is on the whole one of attraction, this will give rise to a tension at the surface of the liquid; this tension will be constant so long as the thickness of the liquid film is greater than the range of molecular attraction. The surface tension will be constant also for curved surfaces, provided that the radius of curvature of the surface is large compared with the range of attraction. These conclusions are true whether we adopt the view of Laplace that the transition from liquid to vapour at the surface is abrupt, or the alternative and more probable theory of Poisson that the density changes gradually at the surface from that of the liquid to that of the vapour. Since it is found experimentally that the surface tension of liquid films is constant down to a thickness of 10^{-6} cms., this gives us an upper limit for the range of attraction.

Another important result reached by Laplace is the equation defining the equilibrium of a liquid surface in terms of its curvature and surface tension (equation 5, p. 7). This equation is the basis of all the methods of measuring surface tension.

When, however, we turn to the discussion of the law of force between molecules, we find that the mathematical theories have, as yet, had little success in describing satisfactorily the forces between the molecules of a liquid. Let us suppose that the force of attraction between two molecules varies with their distance apart z, according to some function $\phi(z)$, then according to Laplace the surface tension and cohesion should be given by

$$\gamma = \pi\rho^2 \int_0^\infty z\psi(z)dz \quad \ldots\ldots\ldots\ldots\ldots\ldots (17)$$

$$K = 2\pi\rho^2 \int_0^\infty \psi(z)dz \quad \ldots\ldots\ldots\ldots\ldots\ldots (18)$$

where ρ is the density of the liquid.

Here $\psi(z)$ is a derived function of $\phi(z)$ and is defined by

$$\psi(z) = \int_z^\infty z \int_z^\infty \phi(z)dz \quad \ldots\ldots\ldots\ldots\ldots\ldots (19)$$

The most simple assumption to make about the mathematical

form of $\phi(z)$ is to postulate a force varying inversely as some power of the distance, namely

$$\phi(z) = z^{-n} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (20)$$

From this it follows that

$$\psi(z) = \frac{z^{3-n}}{(3-n)(1-n)} \quad \ldots\ldots\ldots\ldots\ldots (21)$$

and

$$K = 2\pi\rho^2 \left[\frac{z^{4-n}}{(4-n)(3-n)(1-n)} \right]_0^\infty \quad \ldots\ldots\ldots (22)$$

But in this expression for the cohesion the quantity in brackets becomes infinite whatever value is given to n. If n is less than 4 then z^{4-n} is infinite when z is infinite ; if n is greater than 4 then the numerator becomes infinite when $z = 0$; also if $n = 4$ the denominator becomes zero, so that the expression for K again becomes infinite.

It would seem, therefore, that the simple inverse power law must lead to absurd results. The difficulty is, however, due to the fact that by setting a lower limit of 0 in the integrals in equations (17) and (18) it is assumed that the atoms have no size, and that the inverse power law holds, no matter how closely they are brought together. We have seen, however, that in the liquid state the molecules are separated by distances which are of the same order of magnitude as their diameter, and that the force between them must change sign during an encounter and become one of repulsion at very close approaches. The function represented by $\phi(z)$ must therefore be more complicated, and gives rise to still more complicated expressions for γ and K.

An approximate method of dealing with the problem has been used by Edser.* He assumes that molecules can approach each other within a limiting distance δ, which is the molecular diameter, and that up to this point the force of attraction is given by an inverse power law $f = c/x^r$. In summing the expressions for cohesion and surface he then sets this distance δ as the lower limit of the integral, and obtains the following expressions for the cohesion and surface tension.

$$K = \frac{2\pi c N^2}{3(r-4)} \frac{1}{\delta^{r-4}}, \quad \gamma = \frac{2\pi c N^2}{16(r-5)} \cdot \frac{1}{\delta^{r-5}} \quad \ldots\ldots\ldots (23)$$

* *Fourth Report on Colloid Chemistry*, H.M. Stationery Office, 1922, p. 40.

where N is the number of molecules in unit volume. From a comparison of values of γ and K, the latter being calculated from latent heats, etc., Edser concludes that the force between molecules varies as the inverse 8th power of the distance. The principal weakness of Edser's theory lies in the wide choice which is available for the values of δ. The various methods of deducing this quantity give results differing by 10% or more.

CHAPTER II

EMPIRICAL RELATIONS BETWEEN SURFACE TENSION, DENSITY, AND TEMPERATURE

Surface Tension and Temperature

THE surface tension of nearly all liquids is found to diminish as the temperature rises; a few exceptions to this rule have been found, notably with molten cadmium* and with the substances giving "liquid crystals," e.g. p-azoxyanisole.† For most substances the temperature coefficient is not large (about $\frac{1}{2}\%$ per degree), and for small temperature intervals surface tension appears to be a linear function of temperature. When, however, observations are made over larger ranges of temperature, as in the classical work of Ramsay and Shields,‡ it is found that the plot of surface tension against temperature exhibits a decided curvature, and that the slope of the curve diminishes rapidly as the critical temperature is approached.

In 1894 van der Waals suggested the following formulæ, based on the theory of corresponding states, to express the variation of surface tension with temperature.§

$$\gamma = K_1 \theta_c V_c^{-\frac{2}{3}} (1 - T_r)^B \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$= K_2 \theta_c^{\frac{1}{3}} P_c \ (1 - T_r)^B \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Here θ_c, V_c, and p_c are the critical temperature, volume, and pressure, T_r is reduced temperature, and K_1, K_2, and B are universal constants which should have the same value for all liquids.

Later, Ferguson‖ showed that the formula

$$\gamma = \gamma_0 (1 - bt)^n \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

would reproduce very accurately the data of Ramsay and Shields over the whole temperature range. The chief differ-

* Bircumshaw, *Phil. Mag.*, 1927 [7], **3**, 1286.
† Jaeger, *Z. f. anorgan. Chem.*, 1917, **101**, 1.
‡ *Phil. Trans.*, 1893, **184**, 647. § *Z. physikal. Chem.*, **13**, 716.
‖ *Phil. Mag.*, 1916 [6], **31**, 37.

ence between Ferguson's equation and that of van der Waals is that the exponent n is regarded as a third variable in the formula; it is noteworthy, however, that the values of this constant were found to be nearly the same for all the liquids studied and ranged only from 1·192 to 1·248.

It has become evident from modern observations* that the surface tensions recorded by Ramsay and Shields are too low since the correction for capillary rise in the wide tube of their apparatus was underestimated. Fortunately their paper contains sufficient data to permit of the calculation of this correction, and it has been shown by Sugden† that the corrected surface tensions are represented accurately by the van der Waals equation in the form

$$\gamma = \gamma_0(1 - Tr)^{\frac{6}{5}} \quad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

The agreement between the observed and calculated values of the surface tension is shown in table 5. The differences show no systematic drift and are of the order of magnitude of the experimental error; this is true for the six "normal" liquids for which data are available up to the critical temperature. This formula has also been tested over a smaller temperature range for a number of other liquids,‡ and is found to hold with the same accuracy.

TABLE 5

Variation of Surface Tension with Temperature

Benzene.				*Chlorobenzene.*			
t.	*γ obs.*	*γ calc.*	*Diff.*	*t.*	*γ obs.*	*γ calc.*	*Diff.*
20	28·88	28·88	0·00	12	34·36	34·21	0·15
61	23·61	23·65	0·04	50	29·83	29·75	0·08
90	20·13	20·05	0·08	81	26·10	26·19	0·09
120	16·42	16·45	0·03	123	21·63	21·50	0·13
150	13·01	12·97	0·04	150	18·55	18·57	0·02
180	9·56	9·64	0·08	180	15·40	15·40	0·00
210	6·45	6·48	0·03	210	12·16	12·35	0·19
240	3·47	3·59	0·12	240	9·30	9·41	0·11
270	1·05	1·06	0·01	270	6·43	6·61	0·18
280	0·36	0·37	0·01	300	4·05	4·01	0·04
				320	2·39	2·25	0·14
				333	1·63	1·46	0·17
$t_c = 288·5$				$t_c = 359·2$			

* Cf. Richards and Coombs, *J. Amer. Chem. Soc.*, 1915, **37**, 1668.
† *J.C.S.*, 1924, **125**, 32. ‡ Sugden, *J.C.S.*, 1924, **125**, 1167.

The data for the three associated liquids, methyl alcohol, ethyl alcohol, and acetic acid, are not expressed by equation 4 as is shown by the curves in fig. 6. Here $\gamma^{\frac{2}{3}}$ is plotted against

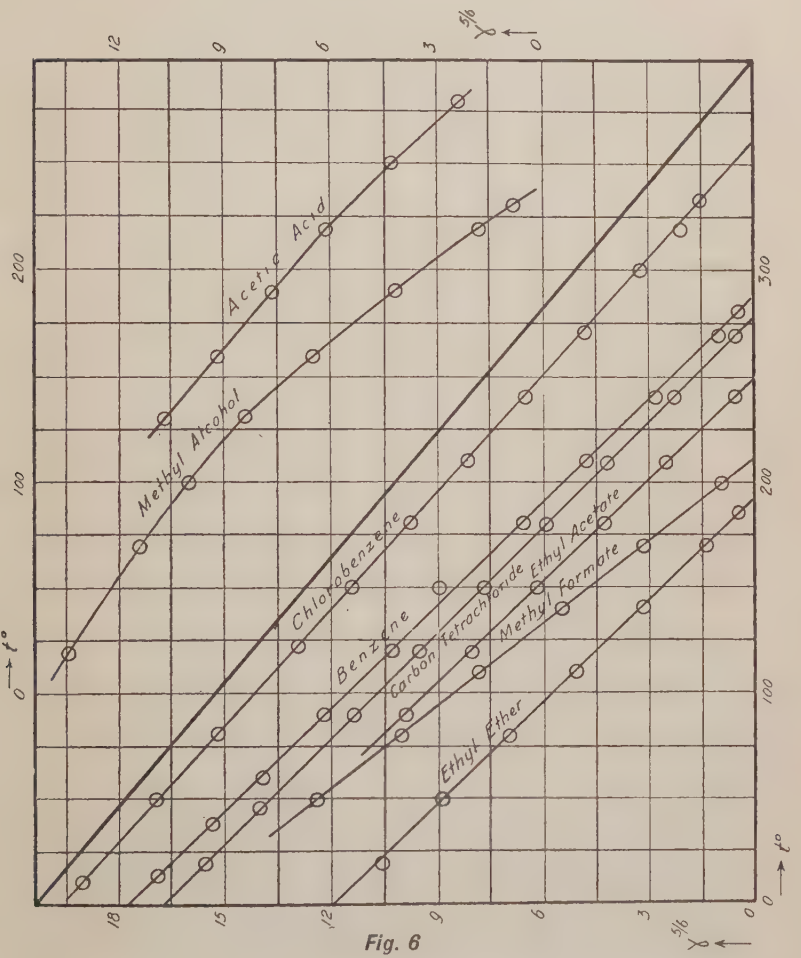


Fig. 6

temperature, so that if this equation holds, the points for one substance should all lie on a straight line. It will be seen that the plot for methyl alcohol and for acetic acid shows a marked curvature whilst the points for the six normal liquids fall accurately on straight lines. (The data for ethyl alcohol give

a curve which nearly coincides with that for methyl alcohol and are therefore not shown.)

In equation (4) γ_0 represents the surface tension of the supercooled liquid at absolute zero, and according to the equations of van der Waals, (1) and (2), should be a function of the critical constants and certain universal constants K_1 and K_2. In table 6 the values of these constants have been calculated from γ_0 and the critical constants given by Young.* K_1 and K_2 are found to be roughly constant, but vary over a range of several

TABLE 6

Van der Waals' Constants

Substance.	γ_0	θ_c	P_c *atm.*	V_c *c.c.*	K_1	K_2
Benzene . .	70·26	561·5	47·89	256·1	5·047	0·646
Chlorobenzene .	70·33	632·2	44·64	307·8	4·763	0·638
Diethyl ether .	55·96	466·8	35·61	281·9	5·155	0·667
Carbon tetrachloride	66·27	556·2	44·98	276·1	5·171	0·637
Methyl formate .	75·85	487	59·25	172·0	4·818	0·635
Ethyl acetate .	65·24	523·1	38·00	286·0	5·414	0·716

per cent for the six liquids studied. It is well known, however, that many other relations between physical properties, deduced from the theory of corresponding states, do not hold accurately but show deviations of this order of magnitude.

Surface Tension and Density

A relation between surface tension and density of a remarkably simple character was discovered by Macleod in 1923, namely:†

$$\gamma = C(D - d)^4 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

Here D and d are the densities of the liquid and vapour, and γ the surface tension at the same temperature. This equation is found to hold for a very large number of liquids giving a constant C which does not vary with the temperature. Some examples are given in table 7 in which the fourth root of this constant is recorded. For normal liquids the Macleod equation holds up to the neighbourhood of the critical temperature and the deviations there found are probably due to errors in the measurement of the surface tensions and densities which are

* *Proc. Roy. Soc.*, Dublin, 1910, **12**, 374.
† *Trans. Faraday Soc.*, 1923, **19**, 38.

difficult to determine with accuracy at these temperatures. Associated liquids, e.g. alcohol, show a small but steady rise of the Macleod constant with temperature.

TABLE 7

Macleod's Constant

Benzene.		*Chloro-benzene.*		*Carbon tetra-chloride.*		*Ethyl alcohol.*	
t.	$C^{\frac{1}{4}}$	*t.*	$C^{\frac{1}{4}}$	*t.*	$C^{\frac{1}{4}}$	*t.*	$C^{\frac{1}{4}}$
20	2·638	12	2·166	20	1·429	20	2·755
61	2·647	81	2·176	46	1·432	80	2·797
90	2·646	123	2·176	90	1·433	110	2·785
120	2·643	180	2·172	120	1·431	140	2·817
150	2·650	210	2·166	150	1·425	170	2·828
180	2·641	240	2·168	180	1·429	200	2·845
210	2·651	270	2·169	210	1·444	230	2·891
240	2·657	300	2·202	240	1·419		
270	2·739	320	2·210	270	1·405		
280	3·372	333	2·299				
$t_c = 288·5$		$t_c = 359·2$		$t_c = 283·1$		$t_c = 243$	

Density and Temperature

If the surface tension, γ, is eliminated between equations (4) and (5), a relation between density and temperature is obtained of the form*

$$D - d = D_0(1 - T\tau)^{\frac{3}{10}} \quad \ldots\ldots\ldots\ldots\ldots(6)$$

This equation is of the same type as that of Verschaffelt.†

$$D - d = mDc(1 - T\tau)^n \ldots\ldots\ldots\ldots\ldots(7)$$

A very stringent test of such equations is given by the data of Young (loc. cit.). Goldhammer,‡ from a discussion of these data, concludes that the exponent "n" in Verschaffelt's equation has the value $\frac{1}{3}$; the exponent $\frac{3}{10}$ (equation 6) gives, however, a still closer agreement between the observed figures and those calculated from equation (6). Some examples are given in table 8, from which it will be seen that the differences are distributed at random and are very small. This equation

* Sugden, *J.C.S.*, 1927, 1780.
† *Commun. of Leiden*, 1896, No. 28.
‡ *Z. physikal. Chem.*, 1910, **71**, 577.

TABLE 8

Variation of Density with Temperature

	Benzene.			*Chlorobenzene.*			*Carbon Tetrachloride.*		
t.	*D*—*d* obs.	*D*—*d* calc.	*Diff.*	*D*—*d* obs.	*D*—*d* calc.	*Diff.*	*D*—*d* obs.	*D*—*d* calc.	*Diff.*
0	0·9000	0·8968	−0·0032	1·1279	1·1237	−0·0042	1·6323	1·6301	−0·0028
40	8568	8571	+0·0003	1·0844	1·0845	+0·0001	1·5540	1·5558	+0·0018
80	8118	8126	+0·0008	1·0411	1·0420	+0·0009	1·4704	1·4722	+0·0018
120	7615	7615	±0·0000	0·9934	0·9944	+0·0010	1·3738	1·3758	+0·0020
160	7012	7008	−0·0004	9412	9416	+0·0004	1·2617	1·2605	−0·0012
200	6250	6246	−0·0004	8804	8795	−0·0009	1·1146	1·1134	−0·0012
240	5137	5169	+0·0032	8056	8057	+0·0001	0·8980	0·8973	−0·0007
280	2854	2743	−0·0111	7342	7378	+0·0036 (270°)			
	$t_c = 288{\cdot}5°$			$t_c = 359{\cdot}2°$			$t_c = 283°$		

holds also for associated liquids at lower temperatures, but deviations are found as the critical temperature is approached, probably owing to changes in the degree of association.

The Eotvos-Ramsay-Shields Equation

The relations between the surface tension, density, and temperature have been shown to be described accurately by equations (4), (5), and (6), or rather by any two of them, for they are interdependent. From these equations a number of other formulæ can be deduced involving all three of these quantities; the most interesting of these is a form of the Eotvos-Ramsay-Shields equation for the change in molecular surface energy with temperature.

If M is the molecular weight, it follows from (6) that

$$\left(\frac{M}{D-d}\right)^{\frac{2}{3}} = \left(\frac{M}{D_0}\right)^{\frac{2}{3}} \frac{1}{(1-T_r)^{\frac{1}{3}}}$$

and combining this with (4)

$$\gamma\left(\frac{M}{D-d}\right)^{\frac{2}{3}} = \frac{\gamma_0 M^{\frac{2}{3}}}{D_0^{\frac{2}{3}}}\left(1-T_r\right) = \left(\frac{\gamma_0 M^{\frac{2}{3}}}{T_c D_0^{\frac{2}{3}}}\right)(T_0 - T)$$

This equation in the form

$$\gamma\left(\frac{M}{D-d}\right)^{\frac{2}{3}} = k'(T_0 - T) \quad \ldots\ldots\ldots\ldots\ldots (8)$$

was first obtained by Katayama* by substituting $D - d$ for D in the equation of Eotvos

$$\gamma\left(\frac{M}{D}\right)^{\frac{2}{3}} = k(T_0 - T) \quad \ldots\ldots\ldots\ldots\ldots (9)$$

* *Sci. Rep. Tohuku Imp. Univ.*, 1916, **4**, 373.

and its relation to the equation of Macleod was pointed out by Ferguson.* Katayama's equation holds accurately up to the critical temperature and in this respect has advantages over the Eotvos equation or the modification due to Ramsay and Shields:

$$\gamma\left(\frac{M}{D}\right)^{\frac{2}{3}} = k(T_0 - T - \delta) \quad \ldots\ldots\ldots\ldots\ldots (10)$$

in which δ is usually about 6°.

It was at one time supposed that the coefficient k in these equations was a constant (about 2·12) for all substances. It is now known, however, that k varies over a wide range for normal liquids, from 1·6 for liquid hydrogen to 5·5 for tristearin, so that molecular weights deduced from the deviation of k from some standard value have no quantitative significance (cf. p. 158).

Total Surface Energy

The work done in producing unit area of new surface of a liquid with a surface tension of γ dynes per cm. is obviously γ ergs, and this is described as the free surface energy. When a new surface is formed the liquid tends to cool and more energy is required to bring it back to its original temperature. From the second law of thermodynamics it follows that the total energy associated with each unit of surface is

$$E_s = \gamma - T\frac{d\gamma}{dT} \quad \ldots\ldots\ldots\ldots\ldots\ldots (11)$$

By differentiating equation (4) and substituting in (11) it is found that

$$E_s = \gamma_0\left(1 + \frac{T_r}{5}\right)^{\frac{1}{6}}(1 - T_r)^{\frac{1}{6}} \quad \ldots\ldots\ldots\ldots\ldots (12)$$

It is often supposed that the total surface energy of a liquid is independent of the temperature; equation (12) shows, however, that it does diminish as the temperature rises, although the change is small as long as T_r is small. At absolute zero the free energy and the total energy are both equal to γ_0; at the boiling point, where T_r is approximately $\frac{2}{3}$, the total surface energy has fallen to $0{\cdot}91\gamma_0$, and above this temperature it decreases rapidly and becomes zero at the critical temperature.

* *Trans. Faraday Soc.*, 1923, **19**, 41, 407.

Molecular Volumes at Constant Surface Tension. The Parachor

Macleod's relation between surface tension and density (5) leads to a new method of comparing molecular volumes, namely, at constant surface tension. Let γ, D, and d be the surface tension, density of liquid, and density of vapour respectively at any temperature, and let D_1 and d_1 be the densities when the surface tension has some arbitrary value γ_1. Then from Macleod's relation,

$$C^{\frac{1}{4}} = \frac{\gamma^{\frac{1}{4}}}{D - d} = \frac{\gamma_1^{\frac{1}{4}}}{D_1 - d_1}$$

so that

$$D_1 - d_1 = (D - d)\frac{\gamma_1^{\frac{1}{4}}}{\gamma^{\frac{1}{4}}}$$

If the standard surface tension γ_1 is suitably chosen, then d_1 is very small compared with D_1 and can be neglected. The molecular volume at this surface tension can then be written

$$\frac{M}{D_1} = \frac{1}{\gamma_1^{\frac{1}{4}}} \cdot \frac{M\gamma^{\frac{1}{4}}}{D - d} = \frac{1}{\gamma_1^{\frac{1}{4}}} MC^{\frac{1}{4}} \quad \ldots\ldots\ldots\ldots\ldots (13)$$

and is therefore *proportional* to the fourth root of Macleod's constant multiplied by the molecular weight. The magnitude of γ_1 merely affects the proportionality factor $1/\gamma_1^{\frac{1}{4}}$; it is therefore convenient to take γ_1 as unity and so define a quantity

$$[P] = \frac{M\gamma^{\frac{1}{4}}}{D - d} = MC^{\frac{1}{4}} \quad \ldots\ldots\ldots\ldots\ldots (14)$$

This quantity is termed the "*parachor*" (from $\pi\alpha\rho\acute{\alpha}$ = set by the side of, and $\chi\acute{\omega}\rho\alpha$ = space).

The chief significance to be attached to a comparison of molecular volumes at constant surface tension instead of at constant temperature, or at constant reduced temperature (e.g. the boiling point), is that this method does make some allowance for the effect upon molecular volumes of the large forces due to molecular attractions. The large internal pressure due to these forces cannot, unfortunately, be measured directly, but the theories of the liquid state considered in chapter I all lead to the conclusion that surface tension and internal pressure are closely related to one another. The general equations of Laplace show indeed that the ratio of the surface tension to the cohesion is a quantity of the order

of magnitude of the range of the molecular forces and in Young's theory is taken as equal to this range. Edser also concludes that this ratio is proportional to the molecular diameter which is of the same order as the range of action of these forces. The range of action and the molecular diameter do not vary much from one substance to another except for very complex substances, and since it is the fourth root of the surface tension which enters into the calculation of the parachor, this quantity must be nearly proportional to the molecular volume at constant internal pressure.

This conclusion is justified by the accurate additive relations which can be traced in the parachors of both organic and inorganic compounds, and with which the remaining chapters of this book are concerned. Further evidence is obtained for the view that the parachor is a true measure of the molecular volume when this constant is compared with the critical volume and with the mean collision area.

Table 9 gives a comparison of critical volumes and parachors for substances ranging in complexity from hydrogen to propyl acetate.

TABLE 9

Parachors and Critical Volumes

Substance.	$[P.]$	V_c	$[P.]/V$
Hydrogen	35·1	46·9	0·75
Methyl formate	138·6	172·0	0·81
Methyl acetate	177·0	227·8	0·78
Benzene	206·3	256·1	0·81
Carbon tetrachloride	219·9	276·1	0·80
Diethyl ether	211·7	281·9	0·75
Methyl propionate	215·0	282·0	0·76
Propyl formate	216·1	284·8	0·76
Ethyl acetate	217·1	286·3	0·76
Chlorobenzene	244·5	307·8	0·80
Methyl isobutyrate	253·3	338·9	0·75
Methyl butyrate	254·2	340·1	0·75
Ethyl propionate	254·8	344·3	0·74
Propyl acetate	256·1	345·3	0·74
		Mean	0·77

The ratio of these two constants varies only a few per cent. from the mean value $[P.]/V_c = 0{\cdot}77$. The critical volumes

used in this table, except that of hydrogen, are due to Young (loc. cit.).

In table 10 the mean collision areas (a) for a number of substances are compared with the two-thirds root of the parachor, which, for symmetrical molecules, should be proportional to the cross-sectional area of the molecule. The values of (a) are taken chiefly from Herzfeld,* whilst the values of the parachor included in brackets have been calculated from the atomic constants, since direct experimental measurements were not available. The ratio $[P.]^{\frac{2}{3}}/a$ is found to be roughly constant for all the substances quoted; better agreement could not be expected, since many of the molecules are far from being

TABLE 10

Parachors and Mean Collision Areas

Substance	$(a) \times 10^{16}$	$[P.]$	$[P.]^{\frac{2}{3}}/a$
Ammonia . .	6·40	60·7	$2·41 \times 10^{16}$
Methane . .	7·72	(73·2)	2·27
Nitrogen . .	7·67	60·4	2·01
Hydrochloric acid .	6·76	67·8	2·46
Hydrobromic acid	7·63	85·4	2·54
Hydriodic acid .	9·26	105·3	2·41
Methyl chloride .	9·67	(110·4)	2·38
Ethyl chloride .	11·94	(149·4)	2·36
Benzene . .	13·83	206·3	2·52
Ethyl acetate .	15·01	217·5	2·41
Propyl acetate .	17·11	256·0	2·30

symmetrical, so that $[P.]^{\frac{2}{3}}$ is only a rough measure of the molecular cross-section.

* *Handbuch der Physik*, XXII, 409, Springer, Berlin, 1926.

CHAPTER III

THE PARACHORS OF ORGANIC COMPOUNDS

The Parachor as an Additive Property

THE first indication that the parachor could be treated as an additive property was obtained by comparing the values of this constant for isomeric substances. For isomerides which differ in structure only by the position of groups or linkages in the molecule, it was found that the parachors were identical within the limits of experimental error. A number of examples of this behaviour are collected in table II.

TABLE II

Parachors of Isomerides

	Esters $C_6H_{12}O_2$[1] [*P.*] *obs.*		[*P.*] *obs.*
i-Amyl formate	293·6	Ethyl propionate	293·6
i-Butyl acetate	295·1	Ethyl *i*-butyrate	292·9
n-Propyl propionate	295·3	Methyl valerate	292·5

Disubstituted Benzene Derivatives[2]

	[*P.*] *obs.*		
	ortho.	*meta.*	*para.*
Xylenes . . .	283·3	283·8	283·8
Nitrotoluenes . .	301·1	300·6	302·8
Chloronitrobenzenes .	299·1	298·9	300·0
Bromonitrobenzenes .	312·9	313·5	313·5
Toluonitriles . .	290·6	295·6	294·4

Geometrical Isomerides[3]

	[*P.*] *obs.*
Methyl cinnamate	373·9
Methyl *allo*cinnamate	376·1
Methyl α-bromocinnamate	426·6
Methyl α-bromo*allo*cinnamate	427·9
Methyl β-bromocinnamate	424·8
Methyl β-bromo*allo*cinnamate	427·5
Methyl mesaconate	341·9
Methyl citraconate	346·1
Methyl fumarate	308·5
Methyl maleate	309·6

(1) Sugden, *J.C.S.*, 1924, **125**, 1185. (2) Sugden and Wilkins, *ibid.*, 1925, **127**, 2517. (3) Sugden and Whittaker, *ibid.*, 1925, **127**, 1868.

When homologous series were examined it was found that a constant difference for CH_2 was shown by all the groups of substances studied. Some examples are set out in table 12. Where the values for several isomerides are known the average parachor only is quoted in the table. Thus the figure 283·9 for the hydrocarbon C_8H_{10} is the mean of the parachors found for ortho-, meta-, and paraxylene, and that for ethyl benzene.

TABLE 12

Homologous Series

Paraffins.			*Benzene hydrocarbons.*		
Formula.	[*P.*] *obs.*	CH_2	*Formula.*	[*P.*] *obs.*	CH_2
C_2H_6	110·5		C_6H_6	206·2	
		40·3			40·0
C_3H_8	150·8		C_7H_8	246·2	
		39·8×3			37·7
C_6H_{14}	270·1		C_8H_{10}	283·9	
		39·2			37·3
C_7H_{16}	309·3		C_9H_{12}	321·2	
		35·7			37·6
C_8H_{18}	345·0		$C_{10}H_{14}$	358·8	
		39·1×2			
$C_{10}H_{22}$	424·2				

Homologous Series—contd.

Esters.			*Ketones.*		
Formula.	*[P.] obs.*	CH_2	*Formula.*	*[P.] obs.*	CH_2
$C_2H_4O_2$	138·1		C_3H_6O	161·5	
		39·2			36·7
$C_3H_6O_2$	177·3		C_4H_8O	198·2	
		38·8			37·5
$C_4H_8O_2$	216·1		$C_5H_{10}O$	235·7	
		38·5			39·2×2
$C_5H_{10}O_2$	254·6		$C_7H_{14}O$	314·1	
		39·2			41·6
$C_6H_{12}O_2$	293·8		$C_8H_{16}O$	355·7	
		38·5			
$C_7H_{14}O_2$	332·3				
		39·3	*Nitriles.*		
$C_8H_{16}O_2$	371·6		*Formula.*	*[P.] obs.*	CH_2
		38·0	CH_3CN	122·2	
$C_9H_{18}O_2$	409·6				38·8×2
			C_3H_7CN	199·9	
					37·0
			C_4H_9CN	236·9	
Amines.					38·1
Formula.	*[P.] obs.*	CH_2	$C_5H_{11}CN$	275·0	
C_3H_9N	178·5				
		39·6×3			
$C_6H_{15}N$	297·3				
		38·8×3			
$C_9H_{21}N$	413·6				

Mean difference for $CH_2 = 39·0$

The constancy of the parachor difference found for a difference in composition of CH_2 is as good as could be expected, and the small variations from the mean value of 39·0 are probably due either to incomplete purification of the substances studied or to small inaccuracies of measurement.

Determination of the Atomic Constants

The atomic parachors of carbon and hydrogen can be obtained simply and logically by combining the mean difference for CH_2 with the data for the paraffin hydrocarbons. If n-times the CH_2 difference is subtracted from the parachor of the hydrocarbon C_nH_{2n+2}, the residue should represent the

effect of two hydrogen atoms. From the data quoted in table 13 it will be seen that this leads to a value for the atomic

TABLE 13

Parachors of Carbon and Hydrogen

Formula.	[*P.*] *obs.*	$n \times CH_2$	$2H$
C_2H_6	110·5	78·0	32·5
C_3H_8	150·8	117·0	33·8
C_6H_{14}	270·1	234·0	36·1
C_7H_{16}	309·3	273·0	36·3
C_8H_{18}	345·0	312·0	33·0
$C_{10}H_{22}$	424·2	390·0	34·2
		Mean	34·3

$H = 17{\cdot}1 \qquad C = 4{\cdot}8$

parachor of hydrogen of 17·1, a figure which receives very satisfactory confirmation from the parachor of liquid hydrogen ([P.] obs. for $H_2 = 35{\cdot}1$). By subtracting the constant for two hydrogen atoms from the mean value for CH_2 the parachor for the carbon atom is found to be 4·8.

This simple method of calculation involves an implicit hypothesis which is of considerable theoretical importance, namely, that the contribution to the parachor of the linkages connecting the carbon and hydrogen atoms is zero. If, however, one attempts to analyse any additive property to give atomic constants it will be found that some hypothesis has to be made about the contribution of the linkages. Thus, suppose the value x is allotted to each single bond, a series of equations for the paraffins can then be developed as follows:

$$C_nH_{2n+2} = nC + (2n + 2)H + (3n + 1)x$$
$$C_{n+1}H_{2n+4} = (n + 1)C + (2n + 4)H + (3n + 4)x$$

where C and H represent the constants for carbon and hydrogen. Subtracting

$$CH_2 = C + 2H + 3x = 39{\cdot}0 \quad \ldots\ldots\ldots\ldots (1)$$

and subtracting $n \times CH_2$ from the value for C_nH_{2n+2}

$$2H + x = 34{\cdot}3 \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

We have, therefore, only two independent equations, (1) and (2), from which to determine the three unknowns C, H, and x. The simplest method of solving the problem is to neglect x

so far as single bonds are concerned and deduce the atomic parachors as shown in table 13. This really means that the single bond is chosen as an arbitrary zero level from which the effect of other structures is measured, and, as we shall see later, both positive and negative contributions due to special structures have been found. The significance of this fundamental hypothesis is discussed later in connexion with electronic theories of valency (p. 110).

Using these standard values for carbon and hydrogen, the atomic parachors of a number of other elements can then be calculated from the parachors of their saturated compounds. Data for chlorine compounds are given in table 14. Here Σ [P.] is the sum of the atomic parachors for all the other elements in the molecule; the contribution made by the chlorine atoms is therefore obtained by subtracting Σ [P.] from [P.] obs.

TABLE 14

Parachor of Chlorine

Substance.	[P.] *obs.*	Σ [P.]	*Cl.*
CCl_4	219·6	4·8	53·7×4
$CHCl_3$	183·2	21·9	53·8×3
CH_2Cl_2	143·0	39·0	52·0×2
$C_2H_2Cl_4$	259·0	43·8	53·8×4
$CH_2Cl{\cdot}CH_2Cl$	189·2	78·0	55·6×2
CH_3CHCl_2	188·5	78·0	55·2×2
C_3H_7Cl	190·2	134·1	56·1
$C_5H_{11}Cl$	269·8	212·1	57·7
		Weighted Mean	54·3

In the same way the parachors of a number of other elements can readily be determined and a list of those commonly found in organic compounds is given in table 15. A fuller list will be found on page 181. It is significant that atomic parachors appear to vary with atomic numbers in the same way as the well-known curve of atomic volumes in the solid state, due to Lothar Meyer. Minima are found at carbon and silicon, and a flat portion of the curve marks the position of the transition elements. This point is discussed more fully in chapter IX, page 181.

TABLE 15

Atomic and Structural Parachors

C	= 4·8	Triple bond	= 46·6
H	= 17·1	Double bond	= 23·2
N	= 12·5	3-membered ring	= 16·7
P	= 37·7	4-membered ring	= 11·6
O	= 20·0	5-membered ring	= 8·5
S	= 48·2	6-membered ring	= 6·1
F	= 25·7		
Cl	= 54·3	O_2 in esters	= 60·0
Br	= 68·0		
I	= 91·0		

Structural Constants

When the parachors of unsaturated substances are examined, it is found that double and triple bonds, and ring structures, produce a considerable increment. This increment is found to be remarkably regular and is constant for a particular link even when the linkage studied connects a variety of different atoms. Thus a double bond gives an increment of about 23·2 units in all the compounds considered in table 16, which includes examples of the links C = C, C = O, C = S, C = N,

TABLE 16

Non-polar Double Bonds

Substance.	*Formula.*	[*P.*] *obs.*	Σ[*P.*]	*Double bond.*
Ethylene	$CH_2=CH_2$	99·5	78·0	21·5
Propylene	$CH_3CH_2=CH_2$	139·9	117·0	22·9
Amylene	$C_3H_7CH=CH_2$	218·2	195·0	23·2
Acetone	$Me_2C=O$	161·5	137·0	24·5
Methyl ethyl ketone	$MeEtC=O$	198·2	176·0	22·2
Diethyl ketone	$Et_2C=O$	236·2	215·0	21·2
Carbon disulphide	$S=C=S$	144·7	101·2	21·8 × 2
Ethyl thiocarbimide	$EtN=C=S$	211·7	160·6	25·5 × 2
Allyl thiocarbimide	$CH_2=CH\cdot CH_2N=C=S$	232·4	165·4	22·3 × 3
Nitrosyl chloride	$ClN=O$	108.1	86·8	21·3
Dimethyl nitrosamine	$Me_2N\cdot N=O$	184·3	157·2	27·1
Diethyl nitrosamine	$Et_2N\cdot N=O$	260·3	235·2	25·1

and N = O. Similarly, it is found that the triple bond in nitriles and in acetylene and its derivatives gives a constant increment of 46·6 units, almost exactly twice the value for a double bond.

From these facts it follows that the parachor is an additive function of a peculiarly simple type, since it can be analysed into two series of constants, one set for the atoms and the other for the linkages present in the molecule. The mean values of these constants are given in table 15. Both series of constants show very little variation over a large range of substances, so that the parachor of a particular compound can be predicted with accuracy by summing the appropriate constants. As an example we may take benzene, C_6H_6.

$C_6 = 6 \times$ 4·8 =	28·8
$H_6 = 6 \times$ 17·1 =	102·6
3 double bonds = 3 × 23·2 =	69·6
6-membered ring =	6·1
[P.] obs. = 206·2	[P.] calc. = 207·1

(Here the Kekulé formula has been used and is found to give good agreement for a large number of benzene derivatives.)

An attempt has been made by Herz* to trace a relationship between the parachor and molecular refraction. It is evident that substances containing a large percentage of carbon and hydrogen, elements which make a constant contribution to both physical properties, must, of necessity, have a nearly constant ratio of parachor to molecular refraction. When, however, the molecule is largely made up of such elements as nitrogen, oxygen, or sulphur, which have variable refraction constants but constant atomic parachors, one would expect to find considerable variations in the value of this ratio, and such indeed is the case as is shown by the data in table 17. The molecular refraction is well known to be influenced largely by the presence of an absorption band in the neighbourhood of the frequency used to determine the refractive index, so that a simple relation between the two constants would not be expected to be valid for more than a narrow range of compounds.

* *Z. f. anorgan. Chem.*, 1927, **159**, 316.

TABLE 17

Parachor and Molecular Refraction

Substance.	$[M.]_D$	$[P.]$	$[P.]/[M.]_D$
Hydrocyanic acid	6·48	81·0	12·50
Acetonitrile	11·11	122·2	11·00
Nitromethane	12·49	132·0	10·57
Acetone	16·15	161·7	10·01
Ethyl sulphate	31·75	313·8	9·88
Ethyl sulphite	31·83	299·7	9·43
Ethyl nitrate	19·30	189·6	9·32
n-Propylamine	19·43	178·5	9·19
Ethylene dichloride	21·07	189·2	8·99
Chloroform	21·40	183·4	8·57
Carbon tetrachloride	26·51	220·0	8·30
Benzene	26·18	206·2	7·88
Carbon disulphide	21·36	144·1	6·75

The constants for ring structures and unsaturated linkages show a steady increase, with the degree of unsaturation being smallest for a six-membered ring and largest for a triple bond. This relation between unsaturation and parachor constant can be expressed by a simple formula in the following way. If x is the number of hydrogen atoms needed to convert the structure into a fully saturated one, and n the number of atoms which form the ring or multiple bond, then the parachor increment [P.] is given by

$$[P.] = 23{\cdot}2x/n$$

The calculated and observed values of $[P.]$ are compared in table 18 and agree within the limits of experimental error. It must, however, be admitted that it is very difficult to give this simple relation any theoretical significance, although it

TABLE 18

Structural Constants and Unsaturation

Linkage.	x.	n.	$[P.]$ *obs.*	$[P.]$ *calc.*
Triple bond	4	2	46·6	46·4
Double bond	2	2	23·2	(23·2)
3-Membered ring	2	3	16·7	15·5
4-Membered ring	2	4	11·6	11·6
5-Membered ring	2	5	8·5	9·3
6-Membered ring	2	6	6·1	7·7

is evident that the parachor increments are intimately connected with the ultimate structures within the molecule which give rise to unsaturation. A rough picture of the state of affairs in an unsaturated molecule can be constructed by the aid of the electronic theory of valency, which indicates that four electrons are shared by the carbon atoms forming a double bond, whilst two only are shared to form a single bond. Unsaturation is therefore associated with a crowding together of the orbits of shared electrons; if it is supposed that the interactions between the shared electrons cause an expansion of the orbits and a separation of the carbon atoms so as to allow for the sharing of a larger number than usual, an explanation of the parachor increment can be obtained. This effect will be greater for a triple bond and smaller for ring structures; in the latter it will diminish as the number of atoms in the ring increases.

Validity of the Additive Relation

In a preliminary survey of the data available in the literature, the parachors of 167 substances were calculated from the observed surface tension and density and compared with the values obtained by summing the appropriate atomic and structural constants.* The difference between the observed and calculated parachors was less than 2% for 145 substances and less than 1% for 104. Concordant measurements of surface tension and density by independent observers were available for 45 substances; all of them gave parachors within 2% of the calculated figures and 36 showed a difference of less than 1%. In later investigations more than 100 other substances have been examined and the same accurate agreement between observed and calculated parachors has been found. Certain of the larger deviations found in the preliminary survey have later been found to be due, either to errors of measurement or to incomplete purification of the specimens measured. Thus the esters of phenylpropiolic acid, calculated from Walden's observations, gave parachors much lower than the calculated value; a reinvestigation of these substances† shows that these substances do not exhibit any real anomaly. The low values given by Walden's specimens are probably due

* Sugden, *J.C.S.*, 1924, **125**, 1177.
† Henley and Sugden (unpublished work).

	[P.] calc.	[P.] obs. Walden.	[P.] obs. H. & S.
Ethyl phenylpropiolate	406·1	375·2	410·3
i-Butyl phenylpropiolate	484·1	424·7	487·1

to the presence of α-bromocinnamic acid in the phenylpropiolic acid used. These acids cannot be separated by crystallisation, and special methods have to be used to obtain the pure acid and to prepare pure esters from it.

A closer examination shows that whilst the parachor is essentially an additive function, some small anomalies, due to constitutional influences, must be recognised. The best example of this effect is the value found for the contribution of the two oxygen atoms in esters, which, as the data in table 19 show, is distinctly less than the predicted value for two oxygen atoms and a double bond, $2 \times 20{\cdot}0 + 23{\cdot}3 = 63{\cdot}2$. For all

TABLE 19

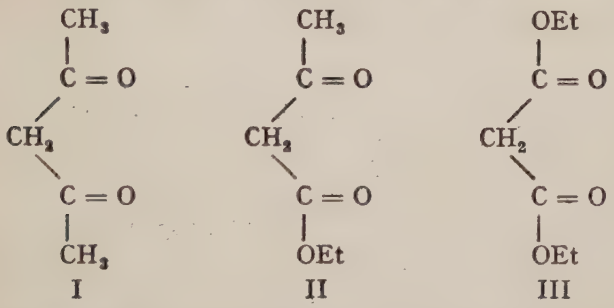
O_2 in Esters

Substance.	*Formula.*	*Observer.*	[P.] obs.	Σ [P.]	O_2
Methyl formate	$C_2H_4O_2$	R. & S.	138·6	78·0	60·6
,, ,,	,,	M. & Sch.	137·7	,,	59·7
Ethyl formate	$C_3H_6O_2$	Sch.	178·4	117·0	61·4
,, ,,	,,	M. & Sch.	177·0	,,	60·0
Methyl acetate	,,	Sch.	177·2	,,	60·2
,, ,,	,,	M. & Sch.	176·7	,,	59·7
Ethyl acetate	$C_4H_8O_2$	R. & S.	217·1	156·0	61·1
,, ,,	,,	Sch.	217·8	,,	61·8
,, ,,	,,	M. & Sch.	215·6	,,	59·6
Methyl propionate	,,	Sch.	215·1	,,	59·1
,, ,,	,,	M. & Sch.	214·9	,,	58·9
n-Propyl acetate	$C_5H_{10}O_2$	Sch.	257·1	195·0	62·1
,, ,,	,,	M. & Sch.	255·0	,,	60·0
Ethyl propionate	,,	Sch.	255·2	,,	60·2
,, ,,	,,	M. & Sch.	254·4	,,	59·4
Methyl butyrate	,,	Sch.	254·1	,,	59·1
,, ,,	,,	M. & Sch.	254·3	,,	59·3
Methyl i-butyrate	,,	Sch.	253·1	,,	58·1
,, ,,	,,	M. & Sch.	253·5	,,	58·5
i-Amyl formate	$C_6H_{12}O_2$	M. & Sch.	293·7	234·0	59·7
,, ,,	,,	M. & K.	293·6	,,	59·6
Ethyl butyrate	,,	Sch.	293·9	,,	59·9
,, ,,	,,	M. & T.	293·0	,,	59·0
,, ,,	,,	R. & Co.	294·2	,,	60·2
					Mean 60·0

Observers: R. & S., Ramsay and Shields; M. & Sch., Morgan and Schwarz; Sch., Schiff; M. & K., Morgan and Kramer; M. & T., Morgan and Thomsson; R. & Co., Richards and Coombs. For full references and a discussion of small corrections applied to the surface tensions recorded by some of these workers, see Sugden, *J.C.S.*, 1924, **125**, 1188.

the substances quoted independent measurements of surface tension and density are available and give parachors agreeing within 1% or less, yet the mean value for O_2 in these esters is 60·0 and differs from the predicted figure by an amount much greater than the errors of measurement.

It is well known that the carbonyl group in esters is very inert when compared with the same structure in aldehydes and ketones, and will not, for example, react with hydroxylamine and semicarbazide. On the other hand, it plays a normal part in numerous condensation reactions, and in general behaviour there is a close similarity between acetyl acetone (I), ethyl acetoacetate (II), and ethyl malonate (III), in which the group COOEt gradually replaces the group $COCH_3$. The



I II III

disturbance of the normal structure of the carbonyl group in esters cannot therefore be very great. It seems probable that there is some interaction between the two oxygen atoms tending to reduce the unsaturation of the double bond which is not indicated by the ordinary formula, but which has a small effect on the parachor.*

Another small constitutional effect has been found for the influence of gem groups, e.g. $R_2C<$, on the stability of ring structures.† Such groups are found to stabilise smaller rings to a marked degree, and this effect is explained by Thorpe and Ingold in the following manner. The groups R, because of their bulk, produce a distortion of the valency linkages which bind them to the carbon atom, making the angle between these links greater than the normal value. The angle between the other pair of valencies therefore tends to become less than normal, and if the carbon atom forms part of a small ring the

* Cf. Smedley, *J.C.S.*, 1909, **95**, 231.
† Cf. Ingold, *ibid.*, 1921, **119**, 305.

strain due to ring formation may be lessened and the ring less easily opened. This obviously corresponds to a decrease in unsaturation and is accompanied by a small fall in parachor. Some examples of this effect are given in table 20.

TABLE 20

Influence of Gem Groups on Unsaturation

Substance.	*Formula.*	[*P.*] *obs.*	[*P.*] *calc.*	*Diff.*
Phorone* . . .	$CH = C(CH_3)_2$ CO $CH = C(CH_3)_2$	367·9	372·2	−4·3
Ethyl cyclopropane 1 : 1-dicarboxylate	$C(COOEt)_2$ CH_2 CH_2	417·1	419·3	−2·2
Ethyl cyclopropane 1 : 1 : 2 : 2-tetra-carboxylate	$C(COOEt)_2$ CH_2 $C(COOEt)_2$	701·1	704·9	−3·8
Ethyl caronate	$CH{\cdot}COOEt$ $(CH_3)_2{\cdot}C$ $CH{\cdot}COOEt$	493·2	496·3	−3·1

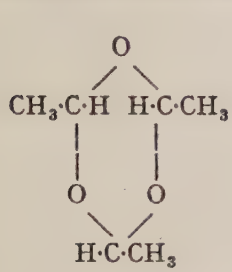
Applications to Structural Problems

Since the parachor is very nearly an additive function of atomic and structural constants, it is obvious that it cannot be used to distinguish between isomerides which differ only by the position of a group or linkage in the molecule. The data already quoted in table 11 show that such isomerides have almost identical parachors. With unsaturated substances no measurable effect is produced by the conjugation of double bonds which has so large an influence upon other physical constants, e.g. refractivity. If, however, unsaturated isomerides differ in structure by the replacement of double bond by a ring, or by the increase in size of a ring, a considerable difference should be found, for the parachors of these structures range from 23·2 for the double bond to 6·1 for a six-membered ring.

A simple example of this effect is furnished by paraldehyde.

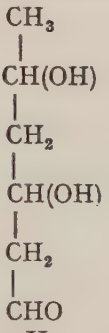
* See also page 49.

This substance, formed by the condensation of three molecules of acetaldehyde, is found to have a parachor of 298·7, which is much less than three times the parachor of acetaldehyde, $3 \times 121{\cdot}2 = 363{\cdot}6$. Some or all of the double bonds in acetaldehyde must therefore be utilised in building up the



[P.] calc. = 300·1

I



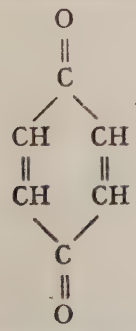
[P.] calc. = 317·2

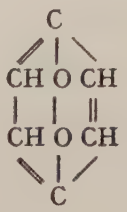
II

paraldehyde molecule, and the good agreement between the observed value and that calculated for the cyclic formula I shows that all three carbonyl groups have taken part in linking up the acetaldehyde residues. If only two of them had been utilised as in the isomeride II, a much larger value would be found for the parachor.

This method has recently been used to investigate the structure of certain quinones, acid chlorides, and diketones, in which tautomerism to a cyclic form has been suggested.* Most of the reactions of the p-quinones are represented by the formula III, but the peroxide formula IV has been suggested on chemical grounds by Graebe,† whilst Hartley and Leonard,‡

III





IV

* Garner and Sugden, *J.C.S.*, 1927, 2877.

† *Annalen*, 1868, **146**, 1. ‡ *J.C.S.*, 1909, **95**, 34.

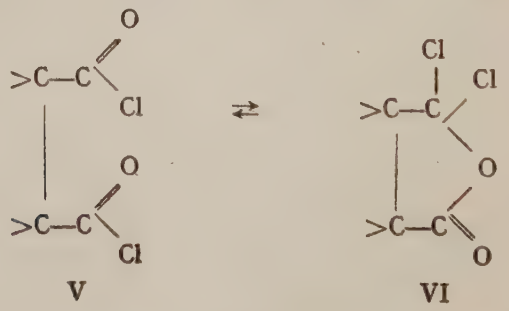
and Haakh,* from a study of absorption spectra, and Binder† from heats of combustion, also prefer formula IV. Measurements of the parachor of benzoquinone and toluquinone give the following figures.

Substance.	[*P.*] *obs.*	[*P.*] *calc.* *Diketone.*	*Peroxide.*
p-Benzoquinone	236·8	236·1	219·0
o-Toluquinone (2-methyl-1 : 4-benzoquinone)	272·0	275·1	258·0

It is evident that these substances have the diketone structure III, and that if tautomerism between III and IV occurs, then the amount of IV present in the fused substance is very small.

The chlorides of dibasic acids would normally be assigned formula V; in some reactions, however, these substances behave as if they possessed the structure shown in formula VI. Thus Auger‡ came to the conclusion on chemical grounds that succinyl chloride was a mixture of the two forms, with the unsymmetrical isomeride in large excess. This view was criticised by Morell,§ who maintained that this substance should be represented by the symmetrical formula. Ott‖ came to the same conclusion, although his determinations of molecular volume seemed to indicate that a mixture of the two forms was present.

Phthalyl chloride offers a still more interesting example, for it has been obtained in two isomeric forms melting at 15°



V VI

* *J. pr. Chem.*, 1910, **82**, 546.
‡ *Ann. Chim.*, 1891, **22**, 36.
‖ *Annalen*, 1912, **392**, 245.
† *Chem. Ztg.*, 1921.
§ *J.C.S.*, 1914, **105**, 1733.

and 88·5°.* Ott and Pfeiffer† have shown that the less stable high-melting modification has probably the unsymmetrical formula, whilst the low-melting form has the symmetrical structure.

The parachors found for these substances are given below. For succinyl chloride it is evident that the liquid substance has the symmetrical formula and cannot contain an appreciable amount of the unsymmetrical modification. The low-melting form of phthalyl chloride gives a parachor slightly lower than that calculated for the symmetrical formula, and must therefore have this structure. The higher melting form gives a smaller parachor, but is a few units larger than that calculated

		[*P.*] *calc.*	
Substance.	[*P.*] *obs.*	*Symmetrical.*	*Unsymmetrical.*
Succinyl chloride	282·6	282·6	267·9
Phthalyl chloride m.p. 15°	373·9	377·5	362·8
Phthalyl chloride m.p. 88·5°	367·8	377·5	362·8

for the unsymmetrical structure. It was found, however, that this modification showed a progressive change in density and a continuous fall in melting point when heated to 90°, so that partial conversion to the other isomeride must have taken place whilst the measurements of surface tension were proceeding. In general, therefore, the parachor confirms the conclusions of Ott and Pfeiffer as to the structure of these substances.

Benzil and its derivatives may be formulated either as diketones (VII) or as peroxides (VIII). From its reactions and yellow colour benzil itself is usually assumed to have the ketonic formula, but certain alkyloxy-derivatives of this substance are white or very pale yellow in colour‡ and are considered by some chemists to be represented more accurately by the heterocyclic formula VIII.§ It should be noted that these white benzil derivatives melt to yellow liquids which may possibly be equilibrium mixtures of the two isomerides.

The parachors of benzil and 2 : 2′-dimethoxybenzil (Irvine's

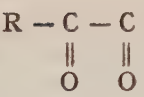
* Ott, loc. cit.; Scheiber, *Ber.*, 1913, **46**, 2368; Csanyi, *Monatsh.*, 1919, **40**, 81.

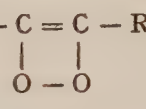
† *Ber.*, 1922, **55**, 413.

‡ Irvine, *J.C.S.*, 1907, **91**, 536.

§ Schonberg and Kraemer, *Ber.*, 1922, **55**, 1174; Schonberg and Malchow, *ibid.*, p. 3746; Schonberg and Bleyberg, *ibid.*, p. 3753.

VII





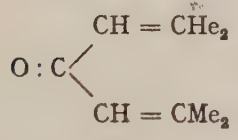
VIII

white benzil) show clearly that the liquid substances do not contain an appreciable amount of the cyclic modification, so

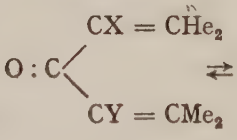
		[P.] *calc.*	
Substance.	[P.] *obs.*	*Diketone.*	*Peroxide.*
Benzil	480·8	476·0	464·4
2 : 2′-Dimethoxybenzil .	596·8	594·0	582·4

that their structure must be represented by the diketone formula VII. If the solid substances possess the peroxide structure it is necessary to assume that the act of solidification is accompanied by a change in structure.

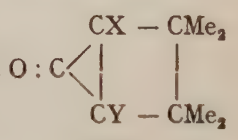
Another structural problem of a similar type is furnished by the tautomerism of derivatives of phorone (IX). These were first studied by Francis and Willson,* and have recently been investigated in detail by Ingold and Shoppee.† If substituents X and Y are introduced into the α positions in the phorone molecule, a rearrangement of valencies may take place to give the bicyclic structure XI. If, however, one of the



IX

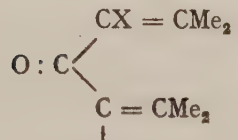


X

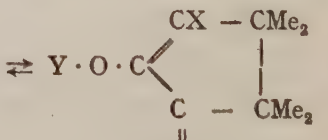


XI

substituent groups is of the form YO-, another type of tautomerism is possible leading to a monocyclic structure, as shown in the formulæ XII and XIII. It will be noted that this



XII



XIII

* *J.C.S.*, 1913, **103**, 2238. † *Ibid.*, 1928, 365, 1662, 1868.

involves the migration of the group Y (or YO-) to a new position in the molecule.

Both of these changes in structure produce ring structures at the expense of double bonds, so that the isomerides which possess the cyclic structures should give lower parachors than would be predicted for the open chain structure X. The parachors of a number of phorone derivatives are collected in table 21. It will be seen that the values found are qualitatively in agreement with the conclusions of Ingold and Shoppee, since most of the substances examined show a considerable negative anomaly.

TABLE 21

*Derivatives of Phorone**

No.	*Substituents.*		*Parachor.*		*Anomaly.*
	X	*Y*	*obs.*	*calc. (open chain).*	
1	H	H	367·9	372·2	−4·3
2	Cl	Cl	427·7	446·6	−18·9
3	Br	Br	463·2	474·0	−10·8
4	H	CH_3COO-	459·4	476·0	−16·6
5	Br	CH_3COO-	506·4	526·9	−20·5
6	Br	CH_3O-	455·3	482·1	−26·8
7	H	C_6H_5COO-	583·9	609·9	−26·0
8	Br	C_6H_5COO-	642·4	660·8	−18·4
9	H	$p\text{-}BrC_6H_4CH_2O-$	630·7	655·0	−24·3
10	Br	$p\text{-}BrC_6H_4CH_2O-$	684·0	705·9	−21·9

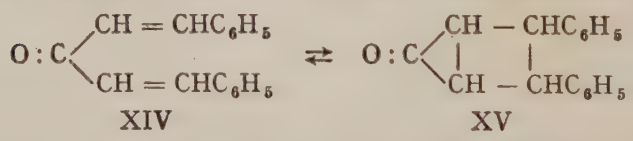
When these anomalies are examined more closely it is found that there are some important discrepancies which still await an explanation. The decrement in the parachor which would be expected for a complete change to the bicyclic structure can be calculated as follows. The constant for the fused ring structure in XI is most probably given by the sum of the values for a 3-membered ring and a 5-membered ring, namely, 16·7 + 8·5 = 25·2. At the same time two double bonds disappear from the molecule so that the change in parachor should be 25·2 − 46·4 = − 21·4. Similarly the change to the monocyclic structure (XIII) gives a change in parachor of 8·5 − 23·2 = − 14·7.

The parachor of phorone (No. 1) is in good agreement with

* Sugden, *J.C.S.*, 1928, 410.

the chemical evidence that this substance possesses essentially the open chain structure. The small anomaly found is probably due to the effect of the two terminal gem-dimethyl groups which would tend to diminish the unsaturation of the adjacent double bonds. Dichloro- and dibromophorone (Nos. 2 and 3) give reactions which indicate that they are tautomeric mixtures of isomerides represented by the structures X and XI, and the parachor anomalies are in harmony with this conclusion. The remainder of the substances listed in the table are derivatives of hydroxyphorone, and from their reactions Ingold and Shoppee conclude that they all have the structure XIII which should give an anomaly of $-14{\cdot}7$. It will be seen, however, that much larger values than this are found, and in some cases the anomaly is even greater than that calculated for the bicyclic structure XI. It may be noted that the low values of the parachor cannot be due to impurities in the specimens examined, for substances Nos. 5, 7, 8, 9, and 10 are solids and were crystallised to constant melting point. Bromomethoxyphorone (No. 6) is a liquid, but three specimens of this substance were used, prepared by different methods, and carefully purified by distillation, and all gave the same parachor. The influence of the terminal gem groups cannot be sufficient to account for the discrepancy (cf. p. 43), for the effect on the stability of the five-membered ring would not cause more than a change of one or two units.

A similar tautomeric change appears to occur with derivatives of distyryl ketone (XIV), which could change into the bicyclic form (XV). The parachor of the unsubstituted ketone indicates that it is wholly in the open chain form ; it



XIV XV

may be noted that there is not even the small negative anomaly found for phorone, since in this case the terminal gem-dimethyl groups are absent. The dibromo derivative gives, however, a marked negative anomaly in its parachor which may be

	[*P.*] *obs.*	[*P.*] *calc.* (*open chain*).	*Anomaly.*
Distyryl ketone . .	564·5	562·0	+ 2·5
Dibromo-distyryl ketone	650·7	663·8	−13·1

interpreted as due to a partial transformation to the bicyclic form.

Another ingenious application of the parachor to solve a structural problem has been made recently by Mumford and Phillips.* In 1922 Mann and Pope chlorinated $\beta\beta$-dichloro-diethylsulphide $(CH_2Cl{\cdot}CH_2)_2S$, and obtained a series of products which were regarded as the tri, tetra, and hexachloro derivatives of diethylsulphide with the formulæ $C_4H_7Cl_3S$, $C_4H_6Cl_4S$, and $C_4H_4Cl_6S$. The compounds containing three and four chlorine atoms were found to possess somewhat anomalous properties, for, unlike the hexachloro-compound, they were very resistant to hydrolysis. This behaviour would not be expected if a chlorine atom is present in a saturated chain in the α position with respect to a sulphur atom. The analyses of these compounds gave low values for hydrogen, and for these reasons Mumford and Phillips concluded that a molecule of hydrochloric acid had been eliminated during the chlorination and that the tri- and tetrachloro-compounds were unsaturated and should be represented by the formulæ $C_4H_5Cl_3S$ and $C_4H_4Cl_4S$, with two hydrogen atoms less than those adopted by the earlier workers. The determination of hydrogen in substances of this type is not easy to carry out with accuracy, but careful repetitions of the analyses gave support to the new unsaturated formulæ.

The elimination of hydrochloric acid might produce, in these compounds, a ring structure or a double bond. Measurements of the parachor showed clearly that the latter hypothesis is the only one which will fit the facts, and that these substances are derivatives of vinyl ethyl sulphide, $CH_2 = CH - S - CH_2 - CH_3$. The observed and calculated parachors are compared in table 22, and it will be seen that the formulæ containing a double bond are the only ones for which the observed parachors give satisfactory agreement with the calculated figures. This conclusion as to the unsaturated character of the tri- and tetrachloro-compounds was confirmed by careful analyses, and by a comparison of other physical properties, e.g. boiling points, molecular volumes, and viscosities.

The constitutions of the substances discussed in this chapter are all represented by the ordinary valency linkages familiar to the chemist, and these structures remained unaltered when expressed in terms of the newer electronic theories of valency.

* *J.C.S.*, 1928, 155.

TABLE 22

Products of Chlorination of ββ-Dichlorodiethylsulphide

Formula.	*Mol. Wt.*	*Parachor. calc.*	*obs.*
Trichloro-compound			
If $C_4H_7Cl_3S$ . .	193·5	350·0	341·9
If $C_4H_5Cl_3S$ containing			
5-membered ring .	191·5	324·3	
4-membered ring .	,,	327·4	338·4
3-membered ring .	,,	332·5	
double bond .	,,	339·0	
Tetrachloro-compound			
If $C_4H_6Cl_4S$ . .	228·0	387·2	277·4
If $C_4H_4Cl_4S$ containing			
5-membered ring .	226·0	361·5	
4-membered ring .	,,	364·6	374·1
3-membered ring .	,,	369·7	
double bond .	,,	376·2	

In a number of other cases the electronic theory predicts a structure which differs from that deduced on the older view, and the parachor has been found to give definite evidence in favour of the newer formulæ. It is therefore necessary at this point to make a digression and consider the physical basis of the electronic theories of valency. This involves a short discussion of the regularities which have been found in emission spectra which have yielded a great deal of detailed information about the structure of atoms.

CHAPTER IV

ATOMS AND SPECTRA

The Nuclear Atom

THE closing years of the nineteenth century were marked by two discoveries which have had a profound influence upon both physics and chemistry. The first of these was the isolation of electrons, particles smaller than the atom and a common constituent of all atoms. The second was the discovery of radioactivity which not only revealed the spontaneous disintegration of certain atoms, but provided in the α-particle a weapon which has been used to probe the innermost recesses of the atom. The ideas which dominate this branch of physics are due largely to Rutherford and his collaborators, and in particular it is Rutherford's nuclear atom model which is the basis of all modern attempts to elucidate the complicated relationships between atom structure and spectra.

Rutherford's conception of the atom is essentially that of a planetary system. The "sun" at the centre is termed the nucleus; it carries practically all the mass of the atom and has a positive electrical charge. Its diameter is known to be about 10^{-13} cm. A comparatively small number of negatively charged electrons are disposed around the nucleus and move in orbits which "occupy" a sphere of 10^{-8} cm. in diameter. Since the electrons are of about the same size as the nucleus it will be seen that the greater part of the volume of what was once regarded as a solid atom consists of nothing but empty space. If we suppose a sodium atom magnified to such a degree that the nucleus appeared to be 1 cm. in diameter, the rest of the atom would consist of 11 electrons, also about 1 cm. across, distributed throughout a sphere with a diameter of a kilometre.

The number of attendant electrons in a neutral atom must obviously be equal to the positive charge on the nucleus; it is usually indicated by the symbol Z and is termed the *atomic*

number. The numerical values of Z for all the atoms in the periodic table have been determined by using a variety of physical phenomena. Hydrogen and helium can be dealt with directly by observing the deflections of the nuclei of these elements in electrical and magnetic fields. For heavier elements the most general method is due to Moseley, who found that the square-root of the characteristic X-ray frequencies emitted by a series of elements is very nearly a linear function of the atomic number. Further evidence is furnished by the scattering of electrons and α-rays by thin films and by the theory of optical spectra. These independent methods all lead to the same result, which may be expressed briefly by stating that the atomic number is fixed by the position of an element in the periodic table. Thus, for hydrogen $Z = 1$, for helium $Z = 2$, and each further step in the table gives an increase of unity in the nuclear charge up to that of the heaviest known atom, uranium, for which $Z = 92$. It has recently been suggested by Flint and Richardson* that there is a real upper limit to atomic number, fixed by the maximum speed which an electron can attain in the innermost orbit ; this limit is reached when $Z = 98$, only six units higher than that of uranium. It should be noted that the determination of atomic numbers has corrected and modified the periodic table of the chemist in some respects. Thus the number of rare earth elements has been defined, and throughout the table it is found that the chemical properties are fixed by the atomic number rather than the atomic weight. A complete table of atomic numbers is included in table 30, page 75.

The nucleus itself is known to be complex and contains electrons as well as positively charged particles; it is the violent expulsion of such particles from the nucleus which gives rise to the phenomenon of radioactivity. In chemical changes, however, the nucleus is undisturbed, and we are only concerned with the disposition and interactions of the extranuclear electrons. It is obviously these electrons only, and particularly such of them as are near the periphery of the atom, which can play any part in the formation of molecules and therefore be concerned in valency linkages. Most of our knowledge of the arrangement and properties of the extranuclear electrons has been obtained by the study of optical and X-ray spectra, from which a very complete scheme of the structure

* *Proc. Roy. Soc.*, 1928 [A], **117**, 637.

of the atom has been deduced. We shall, therefore, at this point, make a brief digression, and consider some of the numerical regularities which have been found to hold accurately for the lines of certain spectra, and which are intimately connected with the problem of atom structure.

Series of Lines in Spectra

The older spectroscopists defined a line in the spectrum by its wave length λ; in modern work the reciprocal of the wave-length, or the wave number, ν, is invariably used, since it simplifies the discussion of the structure of spectra. The wave number means physically, the number of vibrations per cm.; as we shall see later it can be interpreted as a measure of a quantity of energy which is related to the structure of the atom from which the light is emitted.

The first important regularity in spectra was discovered by Balmer as long ago as 1885. He found that a number of lines in the spectrum of hydrogen were related to one another, since their wave lengths were all given accurately by a simple formula. This formula in its modern form may be written

$$\nu = 109678{\cdot}8\left(\frac{1}{2^2} - \frac{1}{m^2}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

By giving m successive integral values of 3, 4, 5, etc., the wave numbers of the lines of this series are predicted accurately as is shown by the data in table 23.

TABLE 23

Balmer's Series

m	ν obs.	ν calc.
3	15233·2	15233·2
4	20564·8	20564·8
5	23032·5	23032·5
6	24373·1	24373·0
7	25181·3	25181·4
8	25706·0	25706·0
∞	—	27419·7

In the spectrum of certain stars this series is well developed, and more than thirty lines have been recorded and measured. As m increases the wave numbers crowd together and approach a certain limit which is termed the convergence frequency.

For the Balmer series this is given by putting $m = \infty$ in the formula and has the wave number 27419·7.

More recently three other series have been found in the hydrogen spectrum which are named after their discoverers, the Lyman, Paschen, and Brackett series. All of them can be represented by a generalised form of the Balmer formula, namely:

$$\nu = \frac{109678{\cdot}8}{n^2} - \frac{109678{\cdot}8}{m^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

The Lyman series in the ultra-violet is obtained by taking $n = 1$ and giving m the values 2, 3, 4, etc. The Paschen series in the infra-red corresponds to $n = 3$ and $m = 4, 5, 6, \ldots$ whilst the Brackett series is given by putting $n = 4$ and $m = 5, 6, 7, \ldots$ There is, however, another method of expressing these regularities which is of great importance, since it leads to a very simple correlation between spectra and atomic structure. Inspection of equation 2 shows that the wave number is given by the difference between two *terms*, and this is found to be true even in much more complex spectra. For hydrogen the terms are given by a very simple rule; it is only necessary to divide the number 109678·8 by the squares of the natural numbers 1, 2, 3, . . . These terms are set out in the second column of table 24; if we subtract the 2nd, 3rd, etc., terms from the first we obtain the wave numbers of the lines of the Lyman series. Similarly by subtracting higher terms from the second term we get the Balmer series, whilst the Paschen and Brackett series may be derived in the same way from the third and fourth terms.

TABLE 24

Terms and Series in the Hydrogen Spectrum

m	*Term.*	*Lyman.*	*Balmer.*	*Paschen.*	*Brackett.*
1	109678·8				
2	27419·7	82259·1			
3	12186·5	97492·3	15233·2		
4	6854·9	102823·9	20564·8	5331·6	
5	4387·2	105291·6	23032·5	7799·3	2467·7
6	3046·7	106632·1	24373·0	9139·8	3808·2
7	2238·3	107440·5	25181·4	9948·2	4616·6
8	1713·7	107965·1	25706·0	10472·8	5141·2
∞	0	109678·8	27419·7	12186·5	6854·9

In the spectra of many other elements similar series of lines have been found which require for their representation a somewhat more complex formula than that of Balmer. In most cases good agreement is obtained by the use of Rydberg's formula :

$$\nu = A - \frac{R}{(m + \mu)^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

and still better agreement can be obtained by means of more elaborate formulæ such as that of Hicks :

$$\nu = A - \frac{R}{\left(m + \mu + \frac{\delta}{m}\right)^2} \quad \ldots\ldots\ldots\ldots\ldots (4)$$

In these equations we have the wave number again expressed as the difference between two terms, the first, constant for the particular series, and the second, diminishing, as m is given successive integral values. μ and δ are small arbitrary constants usually less than 1, and R is a universal constant, known as Rydberg's constant, which occurs in all formulæ for series spectra and has the value 109737. It is thus almost exactly the same as the first term of the hydrogen spectrum, and this remarkable fact is simply explained in terms of theories of atomic structure (cf. p. 63).

In many cases it has been found that the spectrum of an element contains four series of lines which are intimately related to one another. These are known as the Sharp, Principal, Diffuse, and Fundamental series. The names are due largely to the appearance of the lines. Thus the Principal series usually includes the brightest lines in the spectrum, whilst the terms Sharp and Diffuse refer to the appearance of the lines of these series when seen in the spectroscope. The Fundamental series is unfortunately named, for there is nothing particularly fundamental about the lines of this series or the terms from which they are derived. As an example of such series we may take the earlier members of the Sharp and Principal series of lithium. Table 25 shows the relation between the lines of these series when a Rydberg formula is used to represent them. Better accuracy can be obtained by means of a formula of the Hicks type, but, as we shall see, the chief interest in such series lies not in the accuracy of any such formula, but in the relations which can be traced between the terms from which the lines are derived. The column headed mS in the table gives the successive terms of the Sharp series

TABLE 25

Sharp and Principal Series of Lithium

Sharp Series $1P - mS$.				*Principal Series* $1S - mP$.			
m.	*mS.*	*ν calc.*	*ν obs.*	*m.*	*mS.*	*ν calc.*	*ν obs.*
1	43407			1	28594	14883	14904
2	16359	12252	12302	2	12533	30944	30926
3	8515	20096	20107	3	7001	36476	36468
4	5209	23402	23395	4	4462	39015	39013
5	3512	25099	25082	5	3091	40386	40387
6	2527	26084	26047	6	2266	41211	41213
∞		28611		∞		43477	

$$\nu = 28611 - \frac{109737}{(m + 0{\cdot}590)^2} \qquad \nu = 43477 - \frac{109737}{(m + 0{\cdot}959)^2}$$

obtained by putting m in the second term of the formula below the table; by subtracting these terms from the convergence frequency the values of ν calc. are obtained.

It should be noted that the convergence frequency for the Sharp series is almost exactly equal to the first term of the Principal series, and similarly that the convergence frequency of the Principal series is practically equal to the first term of the Sharp series. This is only one example of a number of relations between the terms of the different series which can be summarised as follows. Let the successive terms of, say, the Sharp series be written $1S$, $2S$, $3S$, . . . mS, and the terms of other series be written in a similar way. Then it is found that all four series are represented by the equations

Sharp Series	$\nu = 1P - mS$
Principal Series	$\nu = 1S - mP$
Diffuse Series	$\nu = 1P - mD$
Fundamental Series	$\nu = 1D - mF$

Thus the Sharp and Diffuse series have the same convergence frequency which is equal to the first term of the Principal series; the limit of the Principal series is the first term of the Sharp series, and the limit of the Fundamental series is the first term of the Diffuse series. It is evident the terms are the significant quantities rather than the wave numbers of the lines; the latter are always given by the difference between a pair of terms. Also, as in the case of hydrogen, other lines are found in the spectrum which are not included in the com-

binations of terms represented by the equations for the four series. There is, however, an important limitation on the way in which the terms may be grouped in pairs to give the wave numbers of lines in the spectrum. If we arrange the terms in the order S, P, D, F, then the so-called combination lines are always due to two terms from adjacent series. Thus, lines corresponding to $2P - mS$ are found, but never $2S - mD$, in which the terms belong to series which are not adjacent. Nor do we find lines corresponding to the difference of two terms of the same series, e.g. $1P - mP$. In fact, if we assign characteristic numbers 1, 2, 3, 4, to the terms S, P, D, F, the selection rule which limits the occurrence of combination lines is given quite simply by stating that the term numbers must differ by ± 1. We shall see later that these properties of the terms have an important bearing on the problem of atom structure (p. 66).

Multiplicities of Spectral Lines

When the lines of the lithium spectrum are examined under high resolution it is found that they are close doublets ; with sodium and potassium the separation between the members of each pair is greater and can be measured accurately. Table 26 gives the wave numbers of the first few members of the Sharp series of sodium ; it will be seen that this series consists of doublets with a constant difference of wave number between each pair. The Principal series of sodium also consists of

TABLE 26

Sodium Doublets. Sharp Series

m	3	4	5	6	7
ν_1	16231	19404	21043	21997	22605
ν_2	16248	19421	21060	22013	22623
Diff.	17	17	17	16	18

doublets, but the separation decreases rapidly as the series is ascended and both sets of lines have the same convergence frequency. The relations between these series of doublets are much more clearly apprehended when the terms are considered instead of the lines. It is found that there is only *one* set of S *terms* but *two* sets of P *terms* which can be represented by

the symbols mP_1 and mP_2. Then, as before, the Sharp series of lines is given by

$$\nu_1 = 1P_1 - mS$$
$$\nu_2 = 1P_2 - mS$$

Since mS has always the same value for a given value of m, each pair will have a constant separation of $1P_1 - 1P_2$. For the Principal series we have the expressions

$$\nu_1 = 1S - mP_1$$
$$\nu_2 = 1S - mP_2$$

Both sets of lines tend to the same convergence frequency $1S$, so that the separation of the pairs diminishes as the series is ascended. Similar relations are found to hold for the D and F series and for other elements in which still higher multiplicities are found. Thus, triplets occur in the spectrum of magnesium, quintets in that of titanium, and octets in that of manganese. When analysed into terms it is found in all cases that the S terms are simple, whilst the P, D, and F terms may be complex, and give rise to multiplets. These regularities are of great significance and play an important part in the discussion of atomic structure (cf. p. 72).

Bohr's Theory of the Hydrogen Atom

According to the classical theories of electricity and magnetism, an electrically charged body, when accelerated, must emit radiation. Many attempts based on this principle were made to account for the regularities in spectra by assuming that the atom contained vibrating electrons, but none of them was successful. Moreover, the very existence of a Rutherford type of atom is inexplicable if the classical theory can be applied without modification to particles as small as electrons. An electron moving in an orbit around a positively charged nucleus is continually accelerated towards the centre of its orbit, and should therefore suffer a constant loss of energy in the form of radiation. Its orbit should thus become smaller and smaller until ultimately it collides with the nucleus.

However, there are very good grounds for believing that the classical theories no longer hold when very small particles are concerned ; in a number of phenomena in which there is an interchange of energy between matter and radiation it is found that these theories break down completely. In particular, the distribution of energy in the spectrum of a " black " body, and the emission of electrons from metals

under the influence of light, can only be accounted for on the view that atoms and electrons do not exchange energy with the ether continuously, but only do so in integral multiples of a definite unit termed by Planck a *quantum*. The size of the quantum depends upon the frequency of the radiation and the amount of energy lost or gained by an atom is given by

$$E = nh\nu \quad \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

Here ν is the frequency of the radiation, n is a whole number, and h is a universal constant, known as Planck's constant which has the value $6{\cdot}545 \times 10^{-27}$ c.g.s. units.

The application of quantum ideas to atomic structure was first made by Bohr in 1913.* He assumed that the hydrogen atom, consisting of one electron revolving around a nucleus with unit positive charge, was only stable when the electron occupied one of a series of specified orbits, and that intermediate orbits were impossible. These stable orbits were defined by a simple rule involving the quantum constant, namely, that the angular momentum of the electron is always an integral multiple of $h/2\pi$. Let us consider for simplicity a circular orbit. Then, if the mass of the electron is m, and its velocity in an orbit of radius r is v, its angular momentum is mvr, and the possible orbits will be given by

$$mvr = nh/2\pi \quad \ldots\ldots\ldots\ldots\ldots\ldots (6)$$

Let the charge on the nucleus be Z (= 1 for hydrogen). The potential energy of the electron will then be $-Ze^2/r$, and has a negative sign because work is required to remove the electron to an infinite distance from the nucleus. The electron has also kinetic energy equal to $\frac{1}{2}mv^2$, and since the force between the electron and nucleus varies inversely as the square of the distance, it is readily shown that

$$\tfrac{1}{2}mv^2 = Ze^2/2r \quad \ldots\ldots\ldots\ldots\ldots\ldots (7)$$

Hence the total energy of the atom, taken as the sum of the potential energy and the kinetic energy, is given by

$$-\frac{Ze^2}{r} + \frac{Ze^2}{2r} = -\frac{Ze^2}{2r} = -\tfrac{1}{2}mv^2 \quad \ldots\ldots\ldots\ldots (8)$$

Now from (6)

$$\tfrac{1}{2}mv = nh/4\pi r$$

and dividing into (7)

$$v = \frac{2\pi Ze^2}{nh}$$

* *Phil. Mag.*, 1913, **26**, 1, 476, 857.

so that the total energy of the atomic system in a state characterised by a given value of n may be written

$$E_n = -\tfrac{1}{2}mv^2 = -\frac{2\pi^2 Z^2 me^4}{h^2} \cdot \frac{1}{n^2} \quad \ldots\ldots\ldots\ldots (9)$$

or

$$E_s = -E_n = \frac{2\pi^2 Z^2 me^4}{h^2} \cdot \frac{1}{n^2} \quad \ldots\ldots\ldots\ldots (9a)$$

E_n, the energy of the system, is therefore negative ; E_s, which is E_n with its sign reversed, is the work which must be done on the system to remove the electron to an infinite distance, and therefore measures the stability of the atom. The most stable orbit is obviously that in which $n = 1$, giving the largest value of E_s.

Bohr's second hypothesis is concerned with the emission of radiation from such an atom. In the stable orbits an electron does *not* radiate, but the loss of radiant energy is supposed to occur when the atom changes from one state to another. If an electron jumps from an outer orbit to an inner orbit then the atom as a whole loses energy, and this is given out in the form of *monochromatic* radiation. The frequency of this radiation is defined by another simple application of the quantum principle, namely :

$$h\nu = E_{n_2} - E_{n_1} \quad \ldots\ldots\ldots\ldots\ldots\ldots (10)$$

This leads immediately to the Balmer formula for the hydrogen spectrum, for from (9)

$$h\nu = \frac{2\pi^2 Z^2 me^4}{h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

and if ν is expressed in wave numbers instead of true frequencies this becomes

$$\nu = \frac{2\pi^2 Z^2 me^4}{ch^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad \ldots\ldots\ldots\ldots (11)$$

where c is the velocity of light.

This expression is of the right mathematical form, for the wave numbers are represented as proportional to differences of the inverse squares of the natural numbers. Moreover, the expression outside the bracket is found to predict the value of the Rydberg constant in terms of the known constants e, m, h, and c. Putting $e = 4{\cdot}774 \times 10^{-10}$ e.s.u., $m = 8{\cdot}97 \times 10^{-27}$ gm., $h = 6{\cdot}545 \times 10^{-27}$ c.g.s. units, and $c = 3 \times 10^{10}$ cm./sec., it is found that $R = 109400$, in good agreement with the experimental value 109678. Indeed, the difference between the observed and calculated figures is less than the uncertainty

in the values of some of the constants used in the calculation. This successful prediction of the value of Rydberg's constant is very convincing evidence in support of Bohr's theory. It may be noted in passing that the small change in this constant on passing from hydrogen to helium and other atoms, is also accounted for on Bohr's theory when the relative masses of nucleus and electron are taken into consideration.

The important conception to be stressed in connexion with Bohr's theory is the idea of different states of the atom associated with different amounts of energy. It is customary to speak of *energy levels* which are defined by the *quantum number n*. This is particularly useful in dealing with more complex atoms in which several electrons may be moving in individual orbits, all characterised by the same quantum number n and all having the same energy level. The innermost level for which $n = 1$ represents the most stable state of the hydrogen atom. When it is excited by heat or by electrical discharges the electron may be ejected from this level and occupy one of the outer orbits. Sooner or later this electron returns to the innermost level and may do so in one jump, or in a series of jumps. The excited gas in the discharge tube will contain atoms at different stages of excitation, and will therefore emit a number of monochromatic rays, each of which corresponds to a transition between two energy levels. We may, if we wish, classify these into groups by collecting together all the frequencies due to transitions terminating at a given level. Thus the lines due to transitions terminating at level 1 will be given by

$$\nu = R\left(\frac{1}{1^2} - \frac{1}{n^2}\right)$$

and are the lines of the Lyman series. It is evident, however, that this classification is somewhat arbitrary, and that a broader view is obtained by regarding all the lines as transitions between energy levels. This corresponds exactly to the analysis of the spectrum into *terms* discussed on page 56. For the hydrogen atom (and for other atoms in which only one electron is concerned with the production of the spectrum) each *term* in the spectrum corresponds to an *energy level* in the atom. We have thus a new interpretation of the term values as a measure of the stability of the atomic state, for they represent the energy required to remove the electron to an infinite distance. In particular the largest numerical term

corresponds to the most stable state of the atom and so indicates the position of the electron in the unexcited atom. This term is known as the " ground," " basic," or " normal " term, and the nature of the normal term gives valuable information as to the position taken up in the atom by the electron which is most easily detached.

The term values are usually quoted in wave numbers for convenience in dealing with spectroscopic data, but they can readily be converted into more familiar energy units. Thus the normal term for hydrogen is 109678 in wave numbers, or in true frequencies 109678 c. The corresponding energy quantum is 109678 ch, and putting in the values of c and h this becomes $2{\cdot}154 \times 10^{-11}$ ergs. Another method of expressing this energy depends upon the fact that if the atom is bombarded with electrons, having a kinetic energy equal to or greater than the energy of the normal term, the gas is ionised. That is, the electron is detached and the gas begins to glow giving out the full series spectrum. The energy of the bombarding electrons can be measured by the voltage which is used to accelerate them, and is given by volts $\times$ charge. Since the charge on the electron is constant, it is customary to speak of the ionising potential V in volts. For a term of wave number X this is given by

$$V = X \cdot \frac{10^{-8} c^2 h}{e} = \frac{X}{8100} \quad \ldots\ldots\ldots\ldots\ldots\ldots (12)$$

Thus, for hydrogen, the normal term corresponds to an ionising potential of 13·54 volts.

General Theory of Spectra

The hydrogen atom is a system of unusual simplicity ; it is only necessary to discuss the motion of two bodies, the nucleus and the electron, and the analytical equations involved are readily solved. Ionised helium, He^+, gives a similar system, but for other atoms we have to deal with the motion of three or more bodies and our analytical methods break down. It is possible, however, to reverse the type of argument used in the case of hydrogen, and, from the regularities found in spectra, to deduce the structure of the atom. In this way a general theory of spectra has been evolved aided by a number of semi-empirical rules which are the beginning of a new quantum mechanics.

Bohr supposes that all atoms contain a series of energy levels

analogous to the levels of the hydrogen atom. In the normal atom some of the innermost levels will be permanently occupied by electrons, and we have therefore to distinguish between two kinds of spectra. If the outer electrons are disturbed and raised to higher levels they will return to the atom giving the lines of the optical spectrum. On the other hand, if an electron from one of the innermost levels is expelled, its place may be taken by an electron already present in the next level higher, or a few levels higher. Since the inner regions of the atom are subjected to very strong forces, these transitions lead to lines of high frequency and constitute the X-ray spectrum of the element. Of course, the two spectra merge into one another as the atomic system becomes simpler, but the distinction between optical and X-ray spectra has much practical convenience.

The study of X-ray spectra gives in the first place an accurate method of fixing the nuclear charge Z according to Moseley's method (cf. p. 54). It has also led to a very convenient nomenclature of the energy levels. It has long been known that the heavier atoms give several important series of X-rays termed the K, L, M, N, etc., series when arranged in descending order of frequency. These series are now known to be due to electronic transitions ending at quantum levels 1, 2, 3, and 4 respectively. Hence the quantum level 1 is very often described as the K level and so on.

The appearance of these series of X-rays, as the atomic number increases, gives some indication of the number of electrons which occupy each level. Thus, all atoms can give a K radiation, the L radiation appears with elements heavier than sodium, whilst the M, N, and O lines appear in this order as the atomic number is increased. These facts, and a great number of others which cannot be discussed in detail here, are in agreement with Bohr's view that the maximum number of electrons which can occupy a level of quantum number n is equal to $2n^2$. In the successive levels we can therefore have the following numbers of electrons.

Quantum number	1	2	3	4	5
Level	K	L	M	N	O
Maxm. No. of electrons	2	8	18	32	50

This leads at once to a scheme of atomic structure for the lighter elements which accounts very well for the periodicity

of their chemical properties (cf. the earlier part of table 31, p. 77). With helium the K level is filled and the next electron in lithium must enter the L level. This level is filled at neon, and in sodium the next electron must enter the M level. When, however, we come to potassium, the M level can still hold ten more electrons, yet it is assumed, as shown in the table, that the next electron enters the N level. This view is, of course, strongly supported by the chemical properties of the element, but on spectroscopical grounds also, it is essential to place the electron in this position. The arguments upon which this and other atomic structures in the table are based will be considered in the following sections.

Azimuthal Quantum Numbers

Whilst the spectrum of hydrogen is accounted for with high accuracy by means of one quantum number, this is not possible for other elements, and three further quantum numbers are needed to define completely the terms of their spectra. The first of these is known as the *azimuthal* quantum number and fixes the series (S, P, D, F, etc.) to which the level belongs. The other two are magnetic quantum numbers and will be considered later.

In the spectra of the alkali metals it seems certain that we are dealing with the transitions of one electron only, and this is often conveniently termed the series electron. If the orbit of this electron lies wholly outside the orbits of the electrons in lower levels, then the core (i.e. the nucleus + inner electrons) should act exactly like a hydrogen nucleus, since its net charge is + 1, and the energy levels should be very similar to those of hydrogen. If, however, the orbit of the series electron passes through the inner orbits, the electron will be seriously perturbed by its closer approach to the nucleus, and the magnitude of the term which corresponds to its energy level will differ appreciably from that of the similar term for hydrogen. Since the terms for hydrogen are given by

$$\nu = \frac{R}{n^2}$$

we can calculate the "effective" quantum number of the terms of the alkali metals by the formula

$$n_{eff.} = \sqrt{R/\nu} \quad \ldots\ldots\ldots\ldots\ldots\ldots (13)$$

The values of $n_{eff.}$ calculated from the largest terms in the spectra of lithium and sodium are given in table 27, together with the most probable values of n, which must, of course, be a whole number.

TABLE 27

Effective Quantum Numbers

		S	*P*	*D*	*F*
Lithium	$n_{eff.}$	1·59	1·96	3·00	4·00
	n	2·00	2·00	3·00	4·00
Sodium	$n_{eff.}$	1·63	2·12	2·99	4·00
	n	3·00	3·00	3·00	4·00

It will be seen that the D and F terms show very little difference between the two values of n. In the P levels the effect of perturbations is already appreciable, and becomes very large in the S levels. From data of this kind Bohr was led to the conclusion that the orbits corresponding to these levels differed markedly in eccentricity. The S level was supposed to be highly elliptical* with the nucleus at one focus, so that for part of its path the series electron penetrated deeply into the orbits of the inner electrons. Next, by applying the quantum principle, Bohr suggested that the number of types of elliptic orbit was limited just as the size of the circular orbits is limited to certain values on the simple theory of the hydrogen atom. It was found that the possible eccentricities are determined by a subsidiary quantum number k which cannot be greater than n. This number k is termed the azimuthal quantum number and the two numbers which define an orbit or an energy level are usually written n_k. The ratio of k to n fixes the ratio of the minor axis of the orbit to the major axis. Thus for orbits of total quantum number 3 there are three levels ; 3_1 in which the minor axis is $\frac{1}{3}$ of the major axis, 3_2 in which the minor axis is $\frac{2}{3}$ of the major axis, and 3_3 which is a circular orbit, since the minor and major axes are equal.

It would seem probable from the evidence discussed in table 27 that the S levels correspond to the most elliptical orbits and that for these orbits $k = 1$. From a comparison of the spectra of elements in related positions in the periodic table, it is possible to extend this rule and correlate definitely the

* An ellipse is only a rough approximation to the shape of the orbit.

type of level with the azimuthal quantum number according to the following scheme.

Type of Level.	*S.*	*P.*	*D.*	*F.*
k	1	2	3	4

Furthermore, if only one electron is concerned in the production of the lines, then the type of the largest term in the spectrum tells us at once the value of k for the least firmly bound electron in the normal atom. This gives very valuable information as to the structure of the atom and enabled Bohr to determine the extent of the transition series of elements and predict correctly the properties of hafnium.

As an example of the application of this principle, we may consider the terms of the spectra of sodium, magnesium, and aluminium given in table 28. The largest term is indicated by an asterisk, and for sodium and magnesium is an S term, whilst for aluminium the P term is the largest. Thus the electron added to the neon structure to form sodium enters a 3_1 orbit, as also does the second electron in magnesium. With aluminium, however, the third electron must enter the 3_2 level, for the normal term is a P term which gives $k = 2$.

TABLE 28

Normal Terms of Sodium, Magnesium, and Aluminium

Sodium.		*Magnesium.*		*Aluminium.*	
1S	41449*	1S	61672*	1S	22933
1P	24493	1P	26621	1P	48169*
2D	12276	2D	15269	2D	15845
3F	6860	—	—	3F	6963

In the next group of the periodic table, potassium and calcium give normal terms of the S type, so that $k = 1$, and the newly added electrons are bound in 4_1 orbits. With scandium we have the first appearance of a normal term of the D type for which $k = 3$. The structures of these elements must therefore be represented by the following scheme.

Energy Levels.	1_1	2_1	2_2	3_1	3_2	3_3	4_1
K .	2	2	6	2	6	–	1
Ca .	2	2	6	2	6	–	2
Sc .	2	2	6	2	6	1	2

In some cases, however, it is found that the quantum number k cannot be decided without ambiguity from the largest terms, and that more than one electron is concerned in the transitions which give rise to the lines of the spectrum. Furthermore, this scheme of energy levels involving two quantum numbers does not give an account of the multiplicities observed in spectra, nor of the behaviour of the lines in a magnetic field. More recently a very comprehensive theory has been developed, chiefly by Hund,* which accounts simply for these and many other regularities found in spectra. This theory has considerable interest from the standpoint of chemistry, for it defines the maximum number of electrons which can occupy each sub-group and thus enables the structure of an atom to be deduced with a high degree of certainty.

Hund's Theory of Spectral Terms

The underlying conception of Hund's theory is really an extension of Bohr's view that the angular momentum of an electron in an atom is an integral multiple of $h/2\pi$. Hund extends this to every possible momentum of the electron and its orbit, and incorporates in his theory the conception of the spinning electron first advanced by Uhlenbeck and Goudsmit.† The first step in Hund's procedure is to assign four quantum numbers to each electron in the atom, whether it is in the excited or the normal state. These numbers are

(a) the principal or total quantum number already described as n in earlier sections.

(b) the serial quantum number l. This is essentially the same as Bohr's azimuthal quantum number k, but is taken as one unit less than k. l may therefore have the values $n - 1$, $n - 2$, $n - 3$, . . . 0. It is termed the serial number since, like k, it is concerned with the series (S, P, D, etc.) to which the level belongs.

(c) the magnetic quantum number m_l. This defines the possible orientation of the orbit in a magnetic field. It can have the values $l, l - 1, l - 2, \ldots -(l - 1), -l$.

* *Z. f. Physik*, 1925, **33**, 345, *Linienspektren und periodisches System der Elemente*, Julius Springer, Berlin, 1927.

† *Naturwiss.*, 1925, **13**, 953.

(d) the spin quantum number m_s, which defines the direction of spin of the electron in a magnetic field. This can have the values $\pm \frac{1}{2}$.

The allocation of these quantum numbers is limited by a very important rule known as Pauli's Exclusion Principle* which may be stated as follows.

In any one atom there cannot exist two electrons with the same four quantum numbers.

This rule defines completely the number of electrons which can occupy a given n_k sub-group. Thus, to take an example, let us consider the 3_2 sub-group. For all the electrons in this group $n = 3$ and $l = k - 1 = 1$. Hence the possible values of m_l are 1, 0, -1. We have now only the spin quantum numbers to allocate, and it is readily seen that only six electrons can occupy this group with the quantum numbers shown below.

n	3	3	3	3	3	3
l	1	1	1	1	1	1
m_l	1	1	0	0	-1	-1
m_s	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$

If we attempted to put more electrons into this group, then since n and l are fixed, they would have quantum numbers identical with one or other of the six arrangements which is contrary to Pauli's principle.

In general, since $m_l = l, l-1, \ldots -(l-1), -l$, this gives $(2l + 1)$ values of m_l, which can each be associated with spin quantum numbers of $\pm \frac{1}{2}$. The maximum number of electrons in such a sub-group is therefore $2(2l + 1)$, or since $l = k - 1$, $2(2k - 1)$. This gives the following scheme for the maximum size of the sub-groups.

Level n_k	1_1	2_1	2_2	3_1	3_2	3_3	4_1	4_2	4_3	4_4
l	0	0	1	0	1	2	0	1	2	3
Maxm. No. of electrons	2	2	6	2	6	10	2	6	10	14

In Bohr's original theory he suggested that the electrons were divided equally between the sub-groups of a given quantum level, e.g. 4 electrons in each of the levels 2_1 and 2_2.

* Pauli, *Z. f. Physik*, 1925, **31**, 765.

In 1924 Main Smith, on chemical evidence, and Stoner, from the levels found in optical and X-ray spectra, independently put forward an unsymmetrical distribution of electrons in the sub-levels which is practically identical with that given above. This scheme, which is an essential part of the modern theory of atomic structure, is now seen to have a theoretical foundation in Pauli's Exclusion Principle, and is supported by a very large amount of experimental evidence.

The next step in Hund's theory is to predict the terms found in the optical spectrum by considering not one electron only, but all the electrons in the atom. This treatment is very general, and covers not only the cases in which one electron is concerned (as in the series spectra of the alkali metals), but the more complex cases in which the atomic states which give the initial and final terms for a line correspond to the movement of two or more electrons. In some spectra it is found that the removal of one electron to a higher level causes a rearrangement of those left behind in the core. This case is also covered by Hund's general method of considering every possible state of the excited atom by summing the quantum numbers of all its electrons. This leads to three resultant quantum numbers which define the condition of the atom as a whole. These three quantum numbers are :—

(a) the serial quantum number L, which is obtained by summing, as vectors, all the m_l values for the individual electrons. This determines the *series* to which the term belongs according to the scheme

$L =$	0	1	2	3	etc.
Series	S	P	D	F	etc.

(b) the spin quantum number S, which is the resultant of the spin vector of the individual electrons. This number determines the *multiplicity* of the terms according to the rule that the multiplicity r is equal to $2S + 1$. Since each new electron adds a new spin vector of $\pm \frac{1}{2}$, we find that Hund's theory gives a simple and convincing explanation of the remarkable relationship between multiplicity and atomic number, which is found throughout the periodic table. This regularity is illustrated by the elements of the first transition series shown in table 29.

TABLE 29

Multiplicities (r) and Atomic Number

K.	*Ca.*	*Sc.*	*Ti.*	*V.*	*Cr.*	*Mn.*	*Fe.*	*Co.*	*Ni.*
	1		1						1
2		2		2				2	
	3		3		3		3		3
		4		4		4		4	
			5		5		5		5
				6		6		6	
					7		7		
						8			

It will be evident when the table of quantum numbers on page 70 is considered, that in a completed sub-group the spin quantum numbers cancel out, owing to the operation of Pauli's principle. It is, therefore, only necessary to consider the electrons in incompleted groups to calculate the value of S and therefore of r. Thus the potassium atom has only one electron in an incomplete group, so that S is always $\pm \frac{1}{2}$ and $r = 2$, in accordance with the experimental fact that the series lines of this element are doublets. With calcium the spin vectors of the two electrons outside the argon shell may be in opposite directions, in which cases $S = 0$, or they may be in the same direction, giving $S = 1$. The corresponding multiplicities are 1 and 3, and the singlet and triplet systems found in the calcium spectrum are thus accounted for. As more electrons are added the multiplicities increase in a regular manner, but an important limit is set by the Exclusion principle. It is evident that the maximum multiplicity is obtained when all the electrons have a spin vector of the same sign, and, until a sub-group is half-filled, this is possible without violating Pauli's principle. When further electrons are added it is necessary, however, to assign to them spin quantum numbers of opposite sign to make all the electrons have different quantum numbers. The occurrence of a maximum multiplicity indicates therefore that a particular quantum group is half-filled. With the series given in table 29 this occurs at manganese which has the structure (cf. table 30, p. 75) :

Level	1_1	2_1	2_2	3_1	3_2	3_3	4_1
No. of electrons	2	2	6	2	6	5	2

The electrons in the 1_1, 2_1, 2_2, 3_1, and 3_2 levels form completed sub-groups and can be neglected. Those in the 4_1 group also form a completed grouplet, but are readily detached and take part in the production of the spectrum. The maximum multiplicity, if all five of the electrons in the 3_3 grouplet can have the same sign for their spin quantum number, is evidently given by $S = 3\frac{1}{2}$ and $r = 8$. (The two electrons originally in 4_1 orbits are also supposed to be excited, so that they can have the same spin quantum number but different k's, making 7 electrons in all which contribute to the multiplicity.) The multiplicity shows, therefore, that the maximum number of electrons in the 3_3 grouplet is $2 \times 5 = 10$, and gives further experimental evidence for the scheme of energy levels shown on page 75.

(c) the inner quantum number j, which is the vectorial resultant of L and S. This number represents the total number of units of angular momentum in the atomic system, and determines the behaviour of the lines of the spectrum in a magnetic field.

It was discovered by Zeeman in 1896 that the lines of a spectrum were split up into a number of separate lines when the radiating atoms are subjected to strong magnetic field. A very large amount of work has been devoted to this subject, and a number of important regularities discovered, which, however, need not be discussed in detail here. In general it is found that the Zeeman effect depends upon the k and j values of the terms which give rise to the lines. Thus, lines due to transitions between initial levels with the same values of k_i and j_i and final levels with the same values of k_f and j_f, are split up in the same way by a magnetic field. The Zeeman effect can therefore be used to determine the k and j values of the levels, and has proved of great value in elucidating the nature of complex spectra. The j's obtained in this way are in complete agreement with those predicted from atomic structures by Hund's theory. Thus, each S level is split up to give two magnetic levels corresponding to $j = \frac{1}{2}$ and $j = -\frac{1}{2}$, and the P, D, and F levels are split up into 6, 10, and 14 magnetic levels in accordance with the values of j obtained theoretically by Hund. For a fuller description of these and other applications of the theory reference may be made to recent papers by Dushman* and Fowler.†

* *Chem. Rev.*, 1928, **5**, 109. † *J.C.S.*, 1928, 764.

A very convenient system of symbols is now used generally to describe the spectral terms or the corresponding atomic state. The series is indicated by a capital letter, e.g. S, P, D, etc., the multiplicity by a number in the upper left-hand corner and the inner quantum number j by a number at the lower right-hand corner, thus ${}^{r}P_{j}$. To avoid the use of fractions $\frac{1}{2}$ is added to j to make it a whole number; since r is even when S is $n + \frac{1}{2}$, this happens with terms of even multiplicity. Thus the term ${}^{2}P_{1}$ corresponds to an atomic state for which $L = 1$, $S = \frac{1}{2}$, and $j = \frac{1}{2}$, and should really be written ${}^{2}P_{\frac{1}{2}}$. With odd multiplicities the true value of j is quoted; thus ${}^{5}F_{1}$ is a term for which $L = 3$, $S = 2$, and $j = 1$.

The Electronic Structure of Atoms

From the analysis of spectra on the lines indicated in the foregoing sections, it is now possible to determine, with a high degree of certainty, the disposition of electrons in the energy levels of all the atoms. The most probable configurations are given in table 30 which includes also the atomic number, and on the right-hand side the type of normal term predicted, on Hund's theory, for the structure indicated in the table. At all the important points where there might be some ambiguity as to the position of the electron last added, the spectroscopic evidence indicates quite clearly in which group it should be placed. The occurrence and development of the transition series of elements, and the number of members of such series, are thus defined with certainty by the types of normal terms found in the spectrum and by the multiplicity relationships. Some minor uncertainties exist as to the positions of certain electrons in more complex atoms. Thus Hund has suggested that the rare earth elements contain two electrons in the 5_3 level, and one in the 6_1 level, instead of the reverse arrangement shown in the table. For platinum and neighbouring elements the spectroscopic evidence seems to indicate that two slightly different arrangements of the electrons can exist. It seems probable, therefore, that the transition elements may exist in more than one configuration, and this is supported by a good deal of chemical evidence as will be shown later. With these reservations the electronic structures given in the table are supported by a very large amount of experimental evidence, and it is very unlikely that they will be modified appreciably by further investigations.

TABLE 30

Atomic Structures

		K	*L*		*M*			*N*				*O*					*P*						*Q*	
	Z	1_1	2_1	2_2	3_1	3_2	3_3	4_1	4_2	4_3	4_4	5_1	5_2	5_3	5_4	5_5	6_1	6_2	6_3	6_4	6_5	6_6	7_1	*Normal Term.*
H	1	1																						S
He	2	2																						S
Li	3	2	1																					S
Be	4	2	2																					S
B	5	2	2	1																				P
C	6	2	2	2																				P
N	7	2	2	3																				P
O	8	2	2	4																				S
F	9	2	2	5																				P
Ne	10	2	2	6																				P
Na	11	2	2	6	1																			S
Mg	12	2	2	6	2																			S
Al	13	2	2	6	2	1																		P
Si	14	2	2	6	2	2																		P
P	15	2	2	6	2	3																		P
S	16	2	2	6	2	4																		S
Cl	17	2	2	6	2	5																		P
A	18	2	2	6	2	6																		P
K	19	2	2	6	2	6	0	1																S
Ca	20	2	2	6	2	6	0	2																S
Sc	21	2	2	6	2	6	1	2																D
Ti	22	2	2	6	2	6	2	2																F
V	23	2	2	6	2	6	3	2																F
Cr	24	2	2	6	2	6	5	1																S
Mn	25	2	2	6	2	6	5	2																S
Fe	26	2	2	6	2	6	6	2																D
Co	27	2	2	6	2	6	7	2																F
Ni	28	2	2	6	2	6	8	2																F
Cu	29	2	2	6	2	6	10	1																S
Zn	30	2	2	6	2	6	10	2																S
Ga	31	2	2	6	2	6	10	2	1															P
Ge	32	2	2	6	2	6	10	2	2															P
As	33	2	2	6	2	6	10	2	3															P
Se	34	2	2	6	2	6	10	2	4															S
Br	35	2	2	6	2	6	10	2	5															P
Kr	36	2	2	6	2	6	10	2	6															P
Rb	37	2	2	6	2	6	10	2	6	0	0	1												S
Sr	38	2	2	6	2	6	10	2	6	0	0	2												S
Y	39	2	2	6	2	6	10	2	6	1	0	2												D
Zr	40	2	2	6	2	6	10	2	6	2	0	2												F
Nb	41	2	2	6	2	6	10	2	6	4	0	1												D
Mo	42	2	2	6	2	6	10	2	6	5	0	1												S
Ma	43	2	2	6	2	6	10	2	6	6	0	1												D
Ru	44	2	2	6	2	6	10	2	6	7	0	1												F
	45	2	2	6	2	6	10	2	6	8	0	1												F

Atomic Structures—contd.

		K	L		M			N				O					P					Q	
	Z	1_1	2_1	2_2	3_1	3_2	3_3	4_1	4_2	4_3	4_4	5_1	5_2	5_3	5_4	5_5	6_1	6_2	6_3	6_4	6_5	6_6	7_1	*Normal Term.*
Pd	46	2	2	6	2	6	10	2	6	10	0	0											S
Ag	47	2	2	6	2	6	10	2	6	10	0	1											S
Cd	48	2	2	6	2	6	10	2	6	10	0	2											S
In	49	2	2	6	2	6	10	2	6	10	0	2	1										P
Sn	50	2	2	6	2	6	10	2	6	10	0	2	2										P
Sb	51	2	2	6	2	6	10	2	6	10	0	2	3										P
Te	52	2	2	6	2	6	10	2	6	10	0	2	4										P
I	53	2	2	6	2	6	10	2	6	10	0	2	5										P
Xe	54	2	2	6	2	6	10	2	6	10	0	2	6										P
Cs	55	2	2	6	2	6	10	2	6	10	0	2	6	0	0	0	1						S
Ba	56	2	2	6	2	6	10	2	6	10	0	2	6	0	0	0	2						S
La	57	2	2	6	2	6	10	2	6	10	0	2	6	1	0	0	2						D
Ce	58	2	2	6	2	6	10	2	6	10	1	2	6	1	0	0	2						H
Pr	59	2	2	6	2	6	10	2	6	10	2	2	6	1	0	0	2						K
Nd	60	2	2	6	2	6	10	2	6	10	3	2	6	1	0	0	2						L
Il	61	2	2	6	2	6	10	2	6	10	4	2	6	1	0	0	2						L
Sa	62	2	2	6	2	6	10	2	6	10	5	2	6	1	0	0	2						K
Eu	63	2	2	6	2	6	10	2	6	10	6	2	6	1	0	0	2						H
Gd	64	2	2	6	2	6	10	2	6	10	7	2	6	1	0	0	2						D
Tb	65	2	2	6	2	6	10	2	6	10	8	2	6	1	0	0	2						H
Ds	66	2	2	6	2	6	10	2	6	10	9	2	6	1	0	0	2						K
Ho	67	2	2	6	2	6	10	2	6	10	10	2	6	1	0	0	2						L
Er	68	2	2	6	2	6	10	2	6	10	11	2	6	1	0	0	2						L
Tu	69	2	2	6	2	6	10	2	6	10	12	2	6	1	0	0	2						K
Yb	70	2	2	6	2	6	10	2	6	10	13	2	6	1	0	0	2						H
Lu	71	2	2	6	2	6	10	2	6	10	14	2	6	1	0	0	2						D
Hf	72	2	2	6	2	6	10	2	6	10	14	2	6	2	0	0	2						F
Ta	73	2	2	6	2	6	10	2	6	10	14	2	6	3	0	0	2						F
W	74	2	2	6	2	6	10	2	6	10	14	2	6	4	0	0	2						D
Re	75	2	2	6	2	6	10	2	6	10	14	2	6	5	0	0	2						S
Os	76	2	2	6	2	6	10	2	6	10	14	2	6	6	0	0	2						D
Ir	77	2	2	6	2	6	10	2	6	10	14	2	6	7	0	0	2						F
Pt	78	2	2	6	2	6	10	2	6	10	14	2	6	9	0	0	1						F
Au	79	2	2	6	2	6	10	2	6	10	14	2	6	10	0	0	1						S
Hg	80	2	2	6	2	6	10	2	6	10	14	2	6	10	0	0	2						S
Tl	81	2	2	6	2	6	10	2	6	10	14	2	6	10	0	0	2	1					P
Pb	82	2	2	6	2	6	10	2	6	10	14	2	6	10	0	0	2	2					P
Bi	83	2	2	6	2	6	10	2	6	10	14	2	6	10	0	0	2	3					P
Po	84	2	2	6	2	6	10	2	6	10	14	2	6	10	0	0	2	4					P
Eka-I	85	2	2	6	2	6	10	2	6	10	14	2	6	10	0	0	2	5					P
Rn	86	2	2	6	2	6	10	2	6	10	14	2	6	10	0	0	2	6					P
Eka-Cs	87	2	2	6	2	6	10	2	6	10	14	2	6	10	0	0	2	6	0	0	0	0	1	S
Ra	88	2	2	6	2	6	10	2	6	10	14	2	6	10	0	0	2	6	0	0	0	0	2	S
Ac	89	2	2	6	2	6	10	2	6	10	14	2	6	10	0	0	2	6	1	0	0	0	2	D
Th	90	2	2	6	2	6	10	2	6	10	14	2	6	10	0	0	2	6	2	0	0	0	1	H
U-X	91	2	2	6	2	6	10	2	6	10	14	2	6	10	0	0	2	6	3	0	0	0	1	K
U	92	2	2	6	2	6	10	2	6	10	14	2	6	10	0	0	2	6	4	0	0	0	1	L

TABLE 31

Electronic Configuration of Atoms

I.	*II.*	*III.*	*IV.*	*V.*	*VI.*	*VII.*	*VIII.*		
H 1								He 2	
Li 2.1	Be 2.2	B 2.3	C 2.4	N 2.5	O 2.6	F 2.7		Ne 2.8	
Na 2.8.1	Mg 2.8.2	Al 2.8.3	Si 2.8.4	P 2.8.5	S 2.8.6	Cl 2.8.7		A 2.8.8	
K 2.8.8.1	Ca 2.8.8.2	Sc 2.8.9.2 (2.8.8.3)	Ti 2.8.10.2 (2.8.8.4)	V 2.8.11.2 (2.8.8.5)	Cr 2.8.13.1 (2.8.8.6)	Mn 2.8.13.2 (2.8.8.7)	Fe 2.8.14.2 (2.8.13.3)	Co 2.8.15.2 (2.8.14.3)	Ni 2.8.16.2
Cu 2.8.18.1 (2.8.17.2)	Zn 2.8.18.2	Ga 2.8.18.3	Ge 2.8.18.4	As 2.8.18.5	Se 2.8.18.6	Br 2.8.18.7		Kr 2.8.18.8	
Rb 2.8.18.8.1	Sr 2.8.18.8.2	Y 2.8.18.9.2 (2.8.18.8.3)	Zr 2.8.18.10.2 (2.8.18.8.4)	Cb 2.8.18.12.1 (2.8.18.8.5)	Mo 2.8.18.13.1 (2.8.18.8.6)	Ma 2.8.18.14.1 (2.8.18.8.7)	Ru 2.8.18.15.1 (2.8.18.8.8)	Rh 2.8.18.16.1 (2.8.18.14.3)	Pd 2.8.18.18.0 (2.8.18.16.2)
Ag 2.8.18.18.1	Cd 2.8.18.18.2	In 2.8.18.18.3	Sn 2.8.18.18.4	Sb 2.8.18.18.5	Te 2.8.18.18.6	I 2.8.18.18.7		Xe 2.8.18.18.8	
Cs 2.8.18.18.8.1	Ba 2.8.18.18.8.2	[Rare Earths]	Hf 2.8.18.32.10.2 (2.8.18.32.8.4)	Ta 2.8.18.32.11.2 (2.8.18.32.8.5)	W 2.8.18.32.12.2 (2.8.18.32.8.6)	Re 2.8.18.32.13.2 (2.8.18.32.8.7)	Os 2.8.18.32.15.1 (2.8.18.32.8.8)	Ir 2.8.18.32.16.1 (2.8.18.32.14.3)	Pt 2.8.18.32.18.0 (2.8.18.32.14.4)
Au 2.8.18.32.18.1	Hg 2.8.18.32.18.2	Tl 2.8.18.32.18.3	Pb 2.8.18.32.18.4	Bi 2.8.18.32.18.5	Po 2.8.18.32.18.6	Eka-I 2.8.18.32.18.7'		Rd 2.8.18.32.18.8	
Eka-Cs 2.8.18.32.18.8.1	Ra 2.8.18.32.18.8.2	Ac 2.8.18.32.18.8.3	Th 2.8.18.32.19.9.2 (2.8.18.32.18.8.4)	Pa 2.8.18.32.20.9.2 (2.8.18.32.18.8.5)	Ur 2.8.18.32.21.9.2 (2.8.18.32.18.8.6)				

For the discussion of many chemical problems it is not necessary to consider the division of the main quantum level into sub-groups, and a condensed table can be used showing the arrangement in the principal quantum levels. This is given in the form of Mendeléeff's table as table 31, by omitting the rare earth elements and adding these as an appendix. In the symbol for the structure of each element the number of electrons in the K, L, M, etc., levels is given in order. Thus the symbol 2.8.7 for chlorine indicates that this element has 2 electrons in the K level, 8 in the L level, and 7 in the M level.

The most obvious feature of chemical interest in this table of electronic configurations is the close correspondence between the number of electrons in the outermost energy level and the position of the element in the table. With the exception of the three transition series (Ti to Cu, Y to Ag, and Ce to Au), the number of electrons in the outermost level is equal to the number of the group in the periodic table to which the element belongs. It is evident that these outer electrons which are least firmly bound must be concerned in the processes which bring about chemical combination, and therefore determine the valency of the atom. The electrons in the highest quantum level are therefore termed "valency electrons," and the residue of the atom, i.e. nucleus + inner electrons, is sometimes termed the core.

TABLE 31a

Electronic Configuration of the Rare Earths

	Z			*Z*	
La	57	2.8.18.18.9.2	Tb	65	2.8.18.26.9.2
Ce	58	2.8.18.19.9.2.	Ds	66	2.8.18.27.9.2
Pr	59	2.8.18.20.9.2	Ho	67	2.8.18.28.9.2
Nd	60	2.8.18.21.9.2	Er	68	2.8.18.29.9.2
Il	61	2.8.18.22.9.2	Tu	69	2.8.18.30.9.2
Sa	62	2.8.18.23.9.2	Yb	70	2.8.18.31.9.2
Eu	63	2.8.18.24.9.2	Lu	71	2.8.18.32.9.2
Gd	64	2.8.18.25.9.2			

Another feature of interest presented by this table is the group of eight electrons which forms the external shell of all the inert gases except helium. These gases are remarkable for their chemical inertness, which would seem to show that an external shell of eight electrons possesses a high degree of

stability. The work required to detach an electron from the atoms of these gases, or the ionisation potential, is also unusually large. Hence an external shell of eight electrons (an " octet ") is supposed to confer stability on molecules as well as atoms, and plays an important part in the development of electronic theories of valency.

Transition Elements

The electron configuration of the transition elements given by Bohr's theory of atomic structure is of special interest, for it can be closely correlated with their chemical and physical properties. Elements belonging to the transition series are often paramagnetic and form coloured ions ; they also exhibit a peculiar type of variable valency changing by single units, e.g. Mn^{II}, Mn^{III}, Mn^{IV}, Fe^{II}, Fe^{III}, etc., whilst the valency of the normal elements usually alters by two units, e.g. SH_2, SO_2, SO_3, PCl_3, PCl_5, etc. For these and other reasons it was suggested by G. N. Lewis in 1916 that these elements contained loosely bound electrons, which might occupy more than one position within the atom, so that their electronic configuration was not uniquely determined. Later Bohr developed this conception in detail and defined the limits of the transition series in terms of the maximum number of electrons which can occupy the energy levels. In general, the occurrence of the transition elements is due to the filling up of energy levels within the atom, which have not been completed before electrons began to occupy places in levels of higher principal quantum number. Thus the atom of argon has a stable group of eight electrons in the M level which can hold as a maximum 18 electrons. In potassium the spectrum shows clearly that the next electron enters the N level leaving the group of eight in the M level intact. The next electron also enters the N level so that the calcium atom has the configuration 2.8.8.2. With the next element, scandium, the additional electron is held rather more firmly in the M level than in the N level, so that this element has the configuration 2.8.9.2 instead of 2.8.8.3. However, scandium undoubtedly forms a trivalent ion which must have the configuration 2.8.8, so that the electrons in the N level are removed almost as easily as the last electron bound in the M level. It is possible that there is a tautomeric equilibrium between the two configurations for the scandium atom, and that although the spectrum reveals only the presence

of the electromeride 2.8.9.2 at high temperatures, under the conditions at which the chemical reactions are studied, some of the scandium atoms in the molecules of scandium compounds may possess the configuration 2.8.8.3. The remaining elements show the orderly completion of the maximum group of 18 electrons in the M level; certain of the electrons in this level can take part in chemical changes giving rise to the peculiar type of variable valency exhibited by these elements. The probable configurations of the ions given by the elements of this series are shown in table 32.

TABLE 32

Configuration of the Ions of the First Transition Series

Sc^{II}	2.8.9	Ti^{II}	2.8.10	V_{II}	2.8.11	Cr^{II}	2.8.12
Sc^{III}	2.8.8	Ti^{III}	2.8.9	V^{III}	2.8.10	Cr^{III}	2.8.11
		Ti^{IV}	2.8.8	V^{IV}	2.8.9	(Cr^{VI}	2.8.8.6)
				(V^{V}	2.8.8.5)		

Mn^{II}	2.8.13	Fe^{II}	2.8.14	Co^{II}	2.8.15	Ni^{II}	2.8.16	Cu^{I}	2.8.18
Mn^{III}	2.8.12	Fe^{III}	2.8.13	Co^{III}	2.8.14			Cu^{II}	2.8.17
Mn^{IV}	2.8.11								
(Mn^{VII}	2.8.8.7)								

The formulæ in brackets in this table indicate the probable configurations of some of those atoms, not as ions but in combination with other atoms. Thus hexavalent chromium shows such a close resemblance to sulphur that it seems highly probable that in the chromates, etc., there are six electrons in the N level which can take part in chemical reactions. For the first five elements of this series it appears, therefore, that certain of the electrons in the M level can be removed by sufficiently powerful chemical forces leaving the stable octet of the argon residue. As the atomic number increases the removal of electrons from this shell becomes more difficult, and the elements iron to copper do not readily exhibit valencies higher than three. The first transition series ends definitely at copper, for the next element, zinc, possesses a stable maximum group of 18 electrons in the N level. The next six elements show the building up of an octet in the N level which is completed at krypton.

The second transition series commences with yttrium and ends with silver; it is precisely similar to the first series, and is due to the development of a group of 18 electrons in the N level after three electrons have been bound in the O level.

This series ends definitely at silver, although the N level can hold as a maximum 32 electrons. A considerable degree of stability must therefore be ascribed to a shell of eighteen electrons, but this group differs in one respect from the octet, since it does not seem to occur as the external shell of a neutral atom. It is true that certain ions possess an outer shell of 18, but in these cases it is probable that the ions are solvated so that the 18 shell is surrounded by electrons from the solvent molecules. In neutral atoms and in compounds such as the arsenates and selenates and in certain complex salts, this group is found as a stable shell only when higher energy levels are occupied by electrons.

The third transition series commences at lanthanum and ends with gold. It corresponds with the filling up of the N level to its maximum of 32, and the formation of a group of 18 in the O level, and thus falls naturally into two parts. The first part comprises the rare earth elements in which the N level, two steps below the periphery of the atom, is being completed, whilst in the trivalent ions of these elements the O level maintains a stable shell of eight. The chemical properties of these elements show only minor variations corresponding to the fact that the outer shells of the atoms have the same configuration. The filling of the N level ends at atomic number 71, and Bohr predicted that the next element would not have the properties of a rare earth, but would resemble zirconium in its chemical and physical behaviour. This prediction was soon brilliantly verified by Hevesy's discovery of hafnium in zirconium minerals; this element was found to have an atomic number of 72, and its resemblance to zirconium is so marked that considerable difficulty was experienced in separating it from this element. The second part of the transition series from hafnium to gold is accompanied by the filling up of the O level to a stable group of 18 electrons, and the elements here show a marked resemblance to the corresponding elements of the first and second transition series.

Finally, thorium, proto-actinium, and uranium show a close resemblance in chemical properties to hafnium, tantalum, and tungsten, and are probably the early members of a fourth transition series. Actinium probably belongs to this series also, but has never been obtained in sufficient amount to enable its chemical properties to be studied in detail.

The distribution of electrons within the atom in sub-divisions of the main quantum levels brings to light a number of interesting correlations with chemical properties. Thus the metals in which the outermost electrons are in highly eccentric orbits, e.g. 2_1, 3_1, 4_1, etc., all give oxides which are strong bases; this is true not only for the alkali metals and the alkaline earths, but also for divalent manganese and iron for instance. When the first sub-group is completed and the next electron enters a group of higher azimuthal quantum number, the oxides are found to be much weaker bases, and in group III of the periodic table we meet with the amphoteric oxides of the type of Al_2O_3. It is evident that the presence of an electron in an outer orbit stabilises the electrons for which $k = 1$, so that they are less easily removed to give the ion of the metal. This leads to the general conclusion that elements in which there are only few electrons in the outermost principal quantum level can readily form positive ions, whilst those in which a sub-group is nearly completed tend to gain electrons and thus form negative ions.

It must be remembered, however, that the electronic distribution defined in the table refers to isolated atoms, for the conditions under which the spectra are excited are in nearly every case such as to decompose compounds into their constituent elements. The electronic configuration of the atom in a compound may be modified, for the influence of the fields of force of the adjacent atoms will modify the values of the energy levels so that, for transition elements, in which the firmness of binding in different levels is nearly the same, a number of configurations may be possible depending upon the nature of the surrounding atoms. Such changes in the disposition of loosely held electrons are particularly to be expected when the electrons take part in a chemical bond by being "shared" with another atom (cf. p. 89). In such a linkage the electron forms a part of the electronic structure of the second atom, and the forces which hold it must be very different from those which are found in the isolated atom. Thus, it seems very probable that whilst the chromium atom, at high temperatures, has the structure 2.8.13.1, deduced from its spectrum, in the chromates it has the alternative structure 2.8.8.6. The change is probably connected with the "sharing" of all the electrons in the outermost level with oxygen atoms, so that under the modified conditions five electrons which, in

the isolated atom, occupy the M level, are raised to the N level and retained there as long as they are " shared." This view is, of course, hypothetical, and we have at present no means of studying directly the energy levels in such molecules by means of spectra, etc. It accounts, however, for many chemical facts in a very simple manner, and until more direct evidence is available may be regarded as a satisfactory working hypothesis.

CHAPTER V

POLAR AND NON-POLAR LINKAGES

The Problem of Molecular Structure

It will be clear from the discussion of atomic structure in the previous chapter, that the atom presents a problem in dynamics which is far too complex to be solved by the mathematical weapons at present available. We can discover regularities in spectra, and correlate these with a system of quantum numbers; yet the physical significance of these numbers is difficult to apprehend, and the mysterious energy relations revealed by the quantum theory remain as one of the unsolved problems of modern physics. Atom dynamics is still largely in the Keplerian stage. We trace numerical regularities in energies and orbits, but we are still waiting for the Newton who will tell us, amongst other things, what processes occur when an electron jump produces radiation, and what conditions determine the energy levels within the atom.

The problem presented by molecules is, of course, still more complex. Some information can be obtained in terms of quanta from the band spectra, which are due to molecules and not to atoms. These have a threefold origin and are characterised by quantum numbers which limit (a) the rotation of the molecule, (b) the vibration of its nuclei, and (c) electronic transitions between energy levels in the molecule. The rotation spectrum gives some important information as to the dimensions of molecules, for it involves the moment of momentum of the molecule about a given axis which is fixed by the dimensions and distribution of mass throughout the molecule. Thus the infra-red band spectra give another means of detecting isotopes. The fine structure of the absorption bands of HCl has long been known to show a series of doublets, with a separation in agreement with that calculated for the difference in mass of the isotopes Cl_{35} and Cl_{37}. The theory of the isotope effect has recently been worked out in detail by

Mulliken, and this method of investigation will probably become an important supplement to the mass-spectrograph in this field of research.

It is, however, only the simplest molecules which can be investigated in this way, for the conditions under which the spectra are excited are usually so violent that the vast majority of the molecules studied by the chemist would be decomposed. The investigation of fluorescence and absorption spectra has not as yet progressed much further than the empirical stage. The most noteworthy results in this field have been obtained by Henri, who has shown that a number of simple Y-shaped molecules, e.g. formaldehyde, acetone, and phosgene, behave as if they were symmetrical and exhibit only two effective moments of inertia in their absorption bands. Naphthalene also gives an absorption spectrum which when analysed indicates that there are only three characteristic vibrations of even this complex molecule which need to be considered. The general results of Henri's investigations seem to indicate that the structure of absorption spectra, whilst complex, is by no means so involved a problem as the number of atoms and linkages in these large molecules would seem to necessitate. When these simplified methods of treatment are discovered in other cases and generalisations are possible, the investigation of absorption spectra promises to become a very valuable source of information about the structure of molecules.

Meanwhile in the facts of chemistry we have a great deal of information about the behaviour of molecules under much milder conditions. In particular, the general laws of chemistry, especially those relating to valency and stereochemistry, give direct and detailed information as to the manner in which atoms group themselves together to form molecules. These facts form the larger part of the raw material from which the electronic theory of valency must be constructed, and are as important as the physical data supplied by the study of spectra, etc. The aim of all electronic theories of molecules must therefore be to frame a hypothesis which shall, on the one hand, be compatible with the atomic structures deduced from spectra, and, on the other hand, be capable of accounting more or less simply for the varied and complex relationships which constitute the chemical properties of the elements.

Valency Linkages. (1) Polar Bonds

The first step towards such a theory is the recognition of certain electrons as " valency " electrons, i.e. those which are concerned in chemical changes. These will probably be found in the outer levels ; atoms cannot penetrate one another, and interaction between them must be confined to the outer shells of electrons. The firmness of binding is usually least for this outer group, and this gives another argument for regarding them as the electrons which take part in chemical reactions. It is customary, therefore, to describe the whole of the electrons in the highest principal quantum level as " valency " electrons, whilst the remainder of the atom (nucleus + inner shells) is termed the " core." This definition does not cover the case of certain transition elements, for here we find electrons which, in the isolated atom, occupy positions in lower levels undoubtedly playing a part in chemical change. If, however, we make the hypothesis suggested on page 82, that these atoms, in their compounds, may possess an alternative structure, they can all be brought within the ambit of the above definition of valency electrons.

The number of the valency electrons (except for the transition elements) is given by the number of the group in the periodic table to which the element belongs. In the first two short periods the building up of a group of eight electrons is clearly seen, and the chemical inertness of the gases in which this group is completed indicates that this " octet " must possess a high degree of stability. In 1916 Kossel* and Lewis† independently suggested that atoms of many elements could attain this outer group of eight electrons, and with it greater stability, by exchanging electrons with other atoms. Thus, if a neutral sodium atom reacts with a neutral chlorine atom by giving up an electron, both will then possess a complete octet as their outer shell. The formation of sodium and chlorine *ions* in this way can be represented by the equation :—

Na	Cl	$\longrightarrow$	Na^+	Cl^-
2.8.1	2.8.7		2.8	2.8.8.

The sodium atom loses its electron in the M level, leaving an octet in the L level, whilst the chlorine atom, by means of the

* *Ann. d. Physik*, 1916, **49**, 229.
† *J. Amer. Chem. Soc.*, 1916, **38**, 762.

extra electron, completes its octet in the M level. The two charged ions are then held together by electrostatic forces to form the compound, sodium chloride.

A linkage of this type is termed, by Lewis, a *polar bond*, and by Langmuir, an *electrovalency*. Substances containing this linkage are found to possess special properties, namely, those usually associated with *salts*. It is not without significance that salts and metals are the only pure substances which, in the fused state, are good conductors of electricity. If salts consist of an assemblage of ions this behaviour is readily accounted for. Other characteristic properties associated with the presence of a polar bond on the molecule are, ready solubility in ionising solvents to give conducting solutions, small solubility in solvents of low dielectric constant, e.g. benzene, and a high melting point and boiling point. There are, however, a number of exceptions to these rules. Thus, many salts are only sparingly soluble in water, e.g. $BaSO_4$, and a few, e.g. $AgClO_4$, are readily soluble in benzene.

The essential feature of such polar molecules is the presence of an electrical dipole, i.e. the electrical centre of gravity of the negative charges of the electrons does not coincide with that of the positive nuclei. Such a separation of electrical charges will produce a considerable field of force around the molecule, and this residual affinity causes the molecules to associate into groups in which the dipoles are arranged in such a manner as to neutralise each other's field. Further, such molecules will tend to set themselves in a definite direction in an electrostatic field and modify its intensity by superimposing upon it their own fields of force. Hence association in the liquid state, and a high dielectric constant, may both be taken as indications of the presence of a polar bond.

The properties of crystals also indicate that salts are made up of ions and not of neutral atoms. From the results of X-ray analysis a broad distinction can be drawn between two types of crystal structure: a typically ionised structure, e.g. that of sodium chloride, in which the ions are closely packed together in the crystal lattice, and a neutral structure, e.g. that of ice, or benzene, in which a much looser packing is found. A theory of the energetics of the crystal lattice has been developed by Born and Landé, which has been found capable of predicting many of the physical properties of

ionised crystals in terms of the electrostatic attractions and repulsions between the ions in the space lattice ; the success of this theory is further evidence for assuming that the units in salts are ions, and not neutral atoms.

It was considered by some of the earlier workers that more direct evidence for the existence of ions in crystals could be obtained from the intensity of the scattered X-rays. To a first approximation the intensity of the scattered ray depends upon the number of electrons in the scattering atom. The largest relative difference in number between the alternative neutral and ionised units in the lattice is furnished by lithium fluoride.

Neutral.		*Ionised.*	
Li	F	Li^+	F^-
2.1	2.7	2	2.8

From an X-ray analysis of this substance, Debye and Scherrer* concluded that the intensities of the scattered rays were in better agreement with the hypothesis that ions, rather than atoms, occupied the crystal lattice. More recent work has shown that the intensity of the scattered X-rays depends upon other factors as well as the number of electrons ; thus Wyckoff† comments on this interpretation of the X-ray data, " In the absence of satisfactory knowledge of the laws of scattering this conclusion does not seem to be entirely justified." In another case, that of sodium fluoride, the presence of ions gives the same number of electrons at every point in the space lattice.

Neutral.		*Ionised.*	
Na	F	Na^+	F^-
2.8.1	2.7	2.8	2.8

If the intensity of the scattered X-rays depends only upon the number of electrons, this uniform structure of the crystal would cause interference between the scattered rays and entirely suppress certain lines in the reflected ray. The odd order reflections from planes with odd indices should be entirely absent, but it is found that these lines can be detected faintly in the reflected X-rays. Potassium chloride is another

* *Physikal. Zeitsch.*, 1918, **19**, 474.

† *The Structure of Crystals*, The Chemical Catalogue Co., New York, 1924, p. 302.

substance of this type which has been very thoroughly studied, and here again the complete symmetry predicted for a simple ionic structure is not found. It is now known that the intensity of scattering depends not only upon the number of electrons, but also upon the firmness with which they are bound in the atom ; hence conclusions based upon the simpler law of scattering may require some modification. In general, the later X-ray evidence seems to indicate that, whilst the units in the space lattice of a salt are primarily ions, the electrons are displaced slightly in such a way as to form a feeble linkage between the atoms.

Valency Linkages. (2) Non-Polar Valencies, Covalencies

The polar theory of chemical combination is obviously a restatement in terms of electrons of the Dualistic theory of Berzelius, and, like the older theory, cannot be accepted as

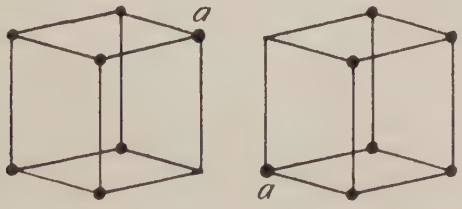
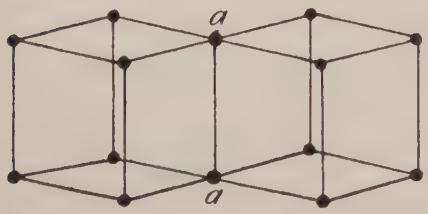


Fig. 7



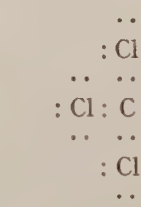
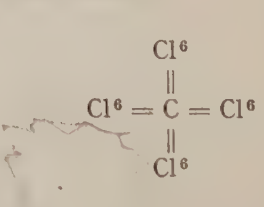
a representation of the linkages in most organic substances. The hydrocarbons, for example, are easily volatilised, and have a low dielectric constant ; they cannot therefore contain an electrical doublet of the type found in sodium chloride. The

general behaviour of organic substances leads inevitably to the conclusion that the valency linkages they possess are neutral in character, and can be formed between atoms which have the same polarity. The electronic interpretation of this type of valency was given by Lewis* in 1916. He suggested that atoms might attain a stable shell of eight electrons, not only by losing or gaining electrons from other atoms, but by "sharing" electrons with an adjacent atom. This conception of sharing was illustrated by the use of cubical atom models as shown in fig. 7.

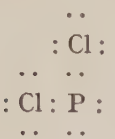
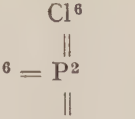
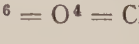
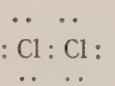
Here two chlorine atoms, with seven valency electrons each, make a stable molecule, in which each chlorine core is surrounded by eight electrons. Two of these electrons, marked *a*, are shared; i.e. they form a part of the electron structure of both atoms.

The cubical atom models used by Lewis are now discarded by most chemists, since they are not in agreement with the stereochemical properties of molecules. In particular, whilst a double bond is readily pictured by placing two cubes face to face, with four electrons shared, it is quite impossible to construct a similar picture of the triple bond by means of cubical atoms. The conception of electron sharing has, however, proved to be a most fruitful contribution to valency theory, and is an essential feature of all modern theories of molecular structure.

An important feature of the sharing of electrons, which was emphasised by Lewis, is the very common appearance of shared electrons in pairs. This is readily seen from an inspection of the electronic formulæ of a few simple substances, e.g. CCl_4, PCl_3, OCl_2, and Cl_2.

Substance.	(*a*) *Electronic Formulæ.*	(*b*)
CCl_4		

* Loc. cit., p. 86.

Substance.	(*a*) *Electronic Formulæ.*	(*b*)
PCl_3		
OCl_2		
Cl_2		

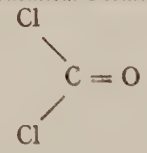
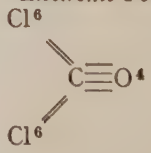
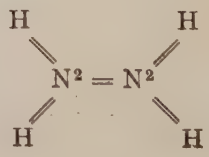
Two methods of writing electronic formulæ are shown. The first (*a*) was given by Lewis, and uses dots to represent the position of the valency electrons. For simple substances this method suffices, but it becomes very tedious to write or read when more complex compounds are considered. For this reason an alternative method, suggested to the author by Dr. J. D. Main Smith, is used throughout this book and is shown at (*b*). Here each shared electron is represented by a line joining the two atoms which share it, whilst unshared electrons are indicated by a superscript number attached to the atomic symbol. The use of these numbers saves a good deal of time in writing and reading the formulæ, and also serves to prevent any confusion between electronic formulæ and ordinary chemical formulæ. It is only with the hydrocarbons, in which all the electrons are shared, that any such confusion between the two types of formulæ may arise, and for these substances, fortunately, it is rarely necessary to use electronic formulæ. In both types of electronic formulæ it should be noted that all the valency electrons are accounted for, so that the symbols for the elements stand for the atomic cores.

The first formula indicates that in carbon tetrachloride the four valency electrons of the carbon atom are each shared with a chlorine atom. The latter provides another electron to form a shared pair, or, to use Lewis' nomenclature, a duplet linkage. In this way all the atoms in the molecule attain an outer shell of eight electrons. With phosphorus, which has five valency

electrons, the group of eight is attained when only three electrons have been bound by duplets, leaving two electrons unshared on the phosphorus atom. With oxygen only two atoms can be attached by means of duplets, and with chlorine only one, without violating the rule that the electrons in the outer shell of each atom must not exceed eight. It is evident that for elements with n valency electrons, where n is greater than 4, the octet rule limits the valency when duplet linkages are used to $8 - n$. If we consider elements in the earlier part of the periodic table, e.g. Be and B, it will be seen that all the valency electrons are used up to form shared pairs before a shell of eight is attained in the central atom. The valency is here given by the number of valency electrons n. It is very useful, therefore, to define a *Normal valency* of the element

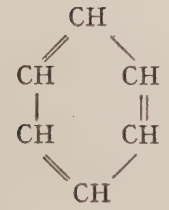
$BeCl_2$	BCl_3
$Cl^6 = Be = Cl^6$	Cl^6 $\parallel$ $Cl^6 = B$ $\parallel$ Cl^6

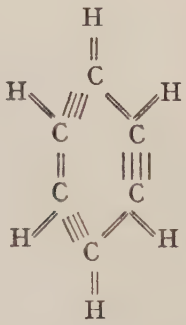
in terms of the number of valency electrons n. This Normal valency is given by n, or $8 - n$, whichever is the less of these two numbers. *For all substances in which the constituent elements exhibit their normal valencies, the electronic formula can be obtained by replacing each bond in the chemical formula by a duplet linkage.* This important generalisation gives an electronic explanation of the structure of the vast majority of organic compounds and of a great many simple inorganic substances. Some examples are given below.

Substance.	*Chemical Formula.*	*Electronic Formula.*
Phosgene		
Hydrazine	$NH_2 \cdot NH_2$	

Substance.	*Chemical Formula.*	*Electronic Formula.*
Acetylene	HC≡CH	H ═ C ≡ C ═ H

Benzene



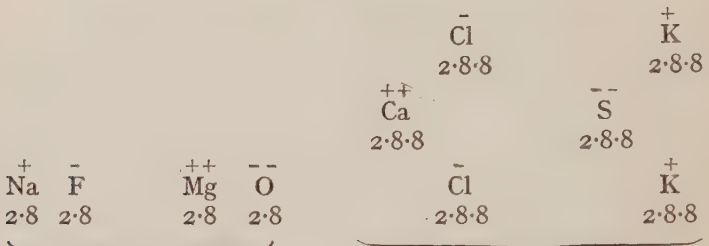


The valency theory of Lewis was extended and discussed in detail by Langmuir,* who added a scheme of atomic structures based upon the conception of a static atom model; this contained an increasing number of cells in successive layers of the atom, each of which could be occupied by an electron. This part of Langmuir's theory is now abandoned by most writers, as it can account for spectra only by endowing electrons which are at rest, or moving in small arcs of an orbit, with all the properties associated with quantised motion in an orbit around the nucleus. Langmuir also traced a number of relations between electronic structure and physical properties, e.g. isomorphism and molecular dimensions, etc., and introduced the term "covalency" for the duplet linkage, which has come into common use. His expression, "electrovalency," to describe the polar linkage of Lewis, is also frequently employed.

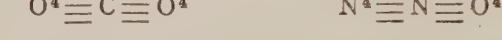
Langmuir points out that isomorphism depends upon a similarity of electron shells, rather than upon a similarity in valency, and thus accounts for a number of cases of isomorphism which were regarded as anomalous. Simple examples are furnished by the isomorphous pairs, NaF, MgO, and $CaCl_2$, K_2S. When the electronic configuration of the ions is

* *Proc. Nat. Acad. Sci.*, 1919, **5**, 252; *J. Amer. Chem. Soc.*, 1919, **41**, 868, 1543; *Science*, 1920, **51**, 605.

considered it is seen that the interchangeable ions in the crystal lattice have the same electronic structure. The second example is interesting as the negative chlorine ion in $CaCl_2$ is replaced by the " isoelectronic " positive potassium ion in K_2S.



For covalent substances also, a very close similarity in physical properties is found for substances which possess the same number of external electrons. Thus, CO_2 and N_2O are *isosteres* and are given by Langmuir the structures



They both have 16 valency electrons arranged in a similar manner, and it is found that their physical properties show a remarkable similarity. Thus, the critical constants, gas viscosities, and the refractive indices and dielectric constants in the liquid state, are very nearly the same for these two substances. From these and many other examples it is concluded that the physical properties are largely determined by the arrangement of external electrons predicted by the octet theory of valency.

It was considered by Lewis that electrons must always be shared in pairs, and that linkages composed of one shared electron could not exist. One argument for this view is found in the fact that the total number of valency electrons in a compound is nearly always an even number, e.g. $CO_2 = 16$, $SH_2 = 8$, $NaCl = 8$, $SnCl_4 = 32$, $PCl_5 = 40$, etc. If duplets and polar bonds are the only possible types of linkage, then this rule should be invariably true. The converse is not, however, necessarily true, for a compound containing an even number of one-electron linkages would still obey the even number rule. It will be shown later that there is a good deal

of evidence for the existence of one-electron linkages, and that these linkages play an important part in the structure of many substances which are not readily accounted for by the Lewis theory. At the present stage it will suffice to mention that a number of odd molecules do exist (i.e. molecules containing an odd number of electrons), e.g. NO = 11, NO_2 = 17, ClO_2 = 19, etc. Further, certain molecules do not contain enough valency electrons to provide duplet linkages between all the atoms. The simplest example is provided by the ion H_2^+, the existence of which is proved by means of positive rays and by its band spectrum; here only one electron is present to hold the hydrogen atoms together. Another example is furnished by diborane, B_2H_6, which is a characteristically non-polar substance, and contains only twelve electrons which must form at least seven linkages to hold the eight atoms together in the molecule. It is evident that at least two of these linkages must contain only one electron.

Electrovalencies and Covalencies. Fajans' Theory

It will be evident from a brief inspection of the periodic table that the elements which show the greatest tendency to form polar linkages are those in which only one or two electrons have to be transferred, i.e. the elements of groups I and II, which readily give positive ions, and those of groups VI and VII, which form negative ions. The halides of other metals are usually found to be non-conductors of electricity in the fused state, and, though they give conducting solutions in certain solvents, there is considerable evidence to show that the ions are produced by interaction with the solvent.

The conductivities of a large number of chlorides in the fused state have been determined by Biltz and Klemm,* and table 33 gives some of their data for the equivalent conductivity at the melting point. This is not, of course, a completely satisfactory method of comparing such data, for the melting points of the substances studied vary over a wide range of temperature. The difference found in the conductivities are, however, so large that the temperature correction is of little importance.

* *Zeit. f. anorgan. Chem.*, 1926, **152**, 281.

TABLE 33

Equivalent Conductivities of Chlorides at the Melting Point

HCl $<10^{-6}$					
LiCl 166	$BeCl_2$ 0·086	BCl_3 0	CCl_4 0		
NaCl 133	$MgCl_2$ 28·8	$AlCl_3$ $1·5 \times 10^{-5}$	$SiCl_4$ 0	PCl_5 0	
KCl 103	$CaCl_2$ 51·9	$ScCl_3$ 15	$TiCl_4$ 0	VCl_4 0	
RbCl 78·2	$SrCl_2$ 55·7	YCl_3 9·5	$ZrCl_4$ —	$NbCl_5$ 2×10^{-7}*	$MoCl_5$ $1·8\times10^{-6}$*
CsCl 66·7	$BaCl_2$ 64·6	$LaCl_3$ 29·0	$HfCl_4$ —	$TaCl_5$ 3×10^{-7}*	WCl_6 2×10^{-6}*
			$ThCl_4$ 16		UCl_4 0·34*

* Specific conductivity.

The mobilities of the metallic ions will also vary, but not over a very wide range. As the data in the table show, the ionised chlorides are sharply marked off from the non-ionised substances, the limit being shown by the stepped line. A noteworthy feature of these results is the manner in which chlorides of metals of higher valency become ionised as the atomic weight of the metallic element increases.

An interesting theory of the conditions which limit the occurrence of polar valencies has been developed by Fajans* on the following lines. Let us consider two ions of opposite sign which approach one another closely. At short distances each will perturb the other's electrons, and, if the disturbance is sufficiently great, the electrons will be diverted into new orbits associated with both atoms, thus producing a covalent

* *Naturwiss.*, 1923, **11**, 163; *Zeit. f. Physik*, 1924, **23**, 1; *Zeit. f. Krystallog.*, 1925, **61**, 18.

linkage. The tendency towards such a change will obviously depend upon the attractive power of the positive ion for electrons, and upon the firmness with which these electrons are held by the negative ion. The intensity of the field around the positive ion is conditioned by its charge and its size. A high charge, therefore, favours the formation of covalencies; this is exemplified by the data in table 33, from which it will be seen that the chlorides of elements of higher valency are usually un-ionised. The same effect is seen when the chlorides of elements of variable valency are compared as in table 34; here the development of higher valencies is accompanied by a large fall in the conductivity. The size

TABLE 34

Influence of Valency on Electrical Conductivity at the Melting Point

Hg_2Cl_2	c. 40	InCl	130	TlCl	46·5	$SnCl_2$	21·9
$HgCl_2$	$2{\cdot}5\times10^{-3}$	$InCl_2$	29	$TlCl_3$	$<2{\cdot}5\times10^{-4}$	$SnCl_4$	0
		$InCl_3$	15				

of the ion also plays a part, for the intensity of the external field will fall off as the diameter of the ion increases. This accounts for the development of polarity in the chlorides of elements of higher valency as the atomic weight of the metal increases; for, in a given family of the periodic table, the size of the atoms increases with the atomic weight. For the negative ion similar considerations can be applied, and it will be seen that increasing charge, and increasing size, both tend towards a looser binding of the external electrons, and favour the formation of covalencies. Thus the tendency towards the formation of non-polar compounds increases on passing from fluorine to iodine (effect of size), or from iodine through selenium to arsenic (effect of charge). The conditions which tend to produce polar or non-polar compounds, when two ions are brought together, can therefore be summarised as follows:

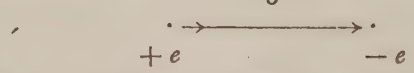
Polar Compounds.	*Non-Polar Compounds.*
Low charge	High charge
Positive ion large	Positive ion small
Negative ion small	Negative ion large.

It should be mentioned that there are a number of compounds which appear to be exceptions to Fajans' rules. Thus,

$ZnCl_2$ and $HgCl_2$ have practically no conductivity in the fused state though they should be highly polar compounds. $CdCl_2$ is, curiously enough, normal, and has a high conductivity. It is well known that many other compounds of these elements are only feebly ionised in solution or in the fused state, e.g. CdI_2, $CdCy_2$, $HgCy_2$, etc. These anomalies may be due to polymerisation. Thus, aluminium chloride is known to have the molecular formula Al_2Cl_6; at its melting point it has only a very small conductivity, but at higher temperatures becomes a much better conductor, indicating that some ions are formed. A closer study of fused salts shows that these substances are often not an assemblage of simple ions, but contain complex ions and associated molecules.* Fajans' theory could therefore not be expected to hold rigidly, but certainly does indicate the main factors which determine the formation of polar molecules.

Partial Polarities. Dielectric Constants

It was emphasised by Lewis in his first paper that a rigid distinction could not be drawn between polar and non-polar substances. Intermediate stages in the development of polarity are clearly indicated by the comparison of many physical properties, e.g. solubility, volatility, and dielectric constant. The characteristic feature of a polar molecule is an electrical dipole, i.e. two equal and opposite electrical charges separated by a short distance, and for the discussion of many physical properties this can be replaced by a simple model consisting of two point charges $+e$ and $-e$ separated by a



distance δ. The effect of such a dipole is measured by its electrical moment μ. A covalent molecule will have zero electrical moment if its electrons are symmetrically arranged around the nuclei, or, more strictly, if the centre of gravity of the charges on the electrons coincides with that of the nuclei. If, however, the shells of electrons are distorted, a small dipole will be developed, which will have a similar, but smaller, effect than that exhibited by the dipoles in ionised molecules. Thus, for example, the hydrogen chloride molecule

* Cf. Chap. VIII, p. 175.

undoubtedly possesses a covalent linkage. In the liquid state this substance is a non-conductor of electricity, and its volatility, its solubility in organic solvents, and its crystal structure all indicate that it belongs to the class of non-polar compounds. Yet its dielectric constant shows clearly that its molecule does contain an electrical dipole, which may be accounted for by a distortion of the electrons around the chlorine atom. This may be indicated diagrammatically in the following manner : (a) represents the structure of a completely non-polar molecule in which the shared electrons are

$$\underset{\text{(a)}}{H : Cl^{6}} \qquad \underset{\text{(b)}}{\overset{+}{H} \quad : Cl^{6}\overset{-}{}}$$

equally held by the hydrogen and chlorine atoms. This is indicated by spacing the dots equally between the symbols for the two atoms. In (b) the shared electrons are supposed to be more closely associated with the chlorine atom so that the latter as a whole carries a small negative charge and the hydrogen atom an equal positive charge. This charge, due to a small displacement of the electrons, may be much smaller than the charge on an ion, in which the electrons are handed over completely to the chlorine atom ; it gives rise, however, to a dipole which produces a measurable effect upon the physical properties of the molecule.

Partial polarities of this kind have been much employed in modern theories of organic chemistry, and a good deal of information about them has recently been obtained by the aid of a theory of dielectric constants due primarily to Debye.* When a molecule possessing an electrical dipole is placed in an electrostatic field it will be affected in two ways by the field. In the first place all the molecules will tend to set themselves in a definite direction in opposition to the field just as magnets do in a magnetic field, fig. 8. This tendency will be opposed by thermal agitation and by the influence of the field of adjacent molecules. It is only under special circumstances that we should therefore expect to get complete orientation. Secondly, the molecules will be stretched or distorted by the

* P. Debye, *Physikal. Zeit.*, 1912, **13**, 97 ; J. J. Thomson, *Phil. Mag.*, 1914, **27**, 757 ; C. P. Smyth, *ibid.*, 1923, **45**, 849 ; 1924, **47**, 530 ; *J. Amer. Chem. Soc.*, 1924, **46**, 2151 ; R. Gans, *Ann. d. Physik*, 1921, **64**, 481.

** Particularly R R[illegible]

field, and so have their moments altered to some extent. The amount of this distortion will obviously depend upon the firmness with which the atoms in the molecule are held together.

The dielectric constant depends upon the total change in the strength of the field due to the presence of the molecules.

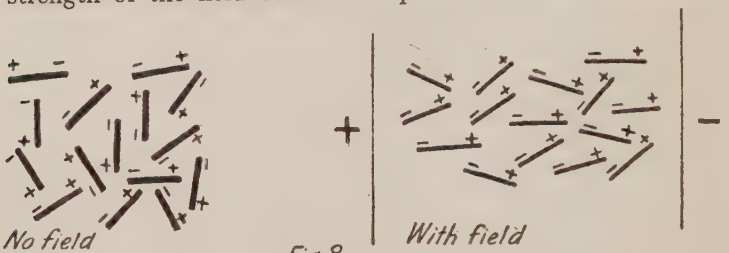


Fig. 8

This can evidently be divided into two parts which we may term a distortion effect and an orientation effect.

Let ϵ be the dielectric constant, M the molecular weight, and d the density of the substance. Then, according to Debye, the electrical moment of a gram-molecule is given by

$$P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d}$$

Dividing this into two terms, we have

$$P = P_\mu + P_D$$

It is the first term only which depends upon the moment μ, of the undistorted molecular dipoles ; hence it is first necessary to find a method of distinguishing between the distortion effect and the orientation effect, i.e. between P_D and $P\mu$.

We can gain some idea of the relative importance of these terms by comparing the values of P for the liquid and solid states. In the solid form no orientation is possible and the electrical moment is entirely due to the distortion term P_D. Two contrasting cases are furnished by water and benzene. For water $P_{\text{liquid}} = 17{\cdot}5$ and $P_{\text{solid}} = 9{\cdot}5$. The large fall indicates that $P\mu$ makes a considerable contribution to P, and that the molecule has therefore a definite electrical moment. On the other hand, for benzene $P_{\text{liquid}} = 26{\cdot}5$, and $P_{\text{solid}} = 26{\cdot}9$; the close agreement between these values shows that $P\mu = 0$, and that the molecule has little or no electrical moment. Another method of distinguishing between P_D and

$P\mu$ is to use an alternating field instead of a steady one. If the frequency of the alternations is sufficiently rapid, the molecules will not have time to set themselves parallel to the field, and a smaller value will be found for the dielectric constant, in which only the distortion effect comes into play. In practice, light waves are used as the alternating field and the quantity measured is the refractive index. The frequency of the light waves used is, however, important. If visible light is employed the vibrations are so rapid that only the lighter electrons can respond to the alternations of the field, and the heavier nuclei are not affected; it is necessary to use infra-red radiation in order to ensure that both electrons and nuclei contribute to the distortion term. For this reason it is convenient to divide the distortion term into two parts which may be termed the electronic effect, P_E, and the atomic effect, P_A. If n is the refractive index for visible light, then

$$P_E = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}$$

If n_r is the refractive index for sufficiently long infra-red rays which will affect both nuclei and electrons, then

$$P_D = P_E + P_A = \frac{n_r^2 - 1}{n_r^2 + 2} \cdot \frac{M}{d}$$

Thus for water $n = 1{\cdot}33$, whence $P_E = 3{\cdot}7$

$n_r = 2{\cdot}00$, whence $P^A + P^E = P^D = 9{\cdot}0$

The latter number is in good agreement with the electrical moment found for ice ($P = 9{\cdot}5$), in which the orientation effect is suppressed and only the distortion term is concerned. For benzene there are no direct observations of n_r available, but it can be shown in the following manner that P_A is small. Since $P = 26{\cdot}5$, and P_E calculated from the refractive index for visible light is $25{\cdot}7$, it follows that $P_A + P\mu = 0{\cdot}8$. This may be taken as the value of P_A since $P\mu$ for benzene is probably zero. In general it is found that P_A is small, and if it cannot be evaluated separately a sufficiently accurate value of $P\mu$ is given by $P - P_E$. Strictly this is equal to $P_A + P\mu$.

We must next consider the conditions which limit the orientation of the molecular dipoles under the influence of a steady field. Here we can distinguish between two effects, namely, (a) dipole association, and (b) the influence of thermal agitation. In a liquid, or a highly compressed gas, the mole-

cules are very close together and the dipoles will tend to arrange themselves in closed chains so as to minimise their external field (fig. 9). It is a suggestive fact that substances containing polar molecules are nearly always associated in the liquid state. In order to obtain the full value of $P\mu$ it is necessary

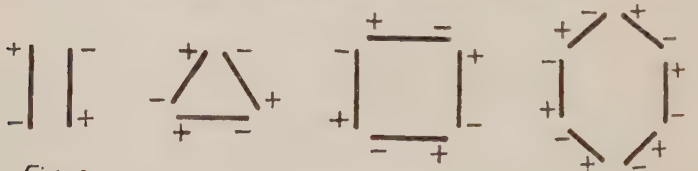


Fig. 9

Dipole association.

to measure the dielectric constant under conditions which ensure that each molecule is well separated from its neighbours, so that dipole association cannot take place. There are two methods which can be employed, namely, measurements in the state of vapour, and in dilute solution in an inert solvent.

It is usually found that, for polar substances, there is a large increase in P when the substance is vaporised. Table 35 gives some data for water and the simpler alcohols. The figures quoted are $P - P_E$, and therefore represent $P_A + P\mu$;

TABLE 35

Electrical Moments in the Liquid and Vapour States

		Water.	*Methyl Alcohol.*	*Ethyl Alcohol.*
$P_A + P\mu$	liquid	13·8	28·8	39·2
	vapour	56·3	54·7	54·9

since P_A is usually small, the main effect is due to $P\mu$. The large increase in this quantity on vaporisation indicates that the aggregates present in the liquid are broken up in the vapour. The values of $P\mu$ in the vapour are nearly constant for these three substances, and represent the effect of the common dipole in the hydroxyl group.

For many substances it is difficult or impossible to make measurements of the dielectric constant of the vapour, and the scope of such investigations has recently been extended to dilute solutions in a suitable solvent. If the solvent is non-polar it is found that the value of $P\mu$ for the solute tends to a limiting value as the solution becomes more dilute, and this

limiting value agrees with that found in the state of vapour. Thus, Krchma and Williams* found for ethyl alcohol, in dilute solution in CCl_4 at 25°, that $P_A + P\mu = 56{\cdot}4$, in good agreement with the value 54·9 as vapour. The agreement is even better when a small correction is made for the difference in temperature between the two observations.

Next we have to consider the effect of thermal agitation upon the orientation of the dipoles. According to Debye the orientation term is related to the moment of the dipoles μ, and the absolute temperature T by the equation

$$P_\mu = \frac{4\pi N\mu^2}{9kT}$$

Here N is Avogadro's number ($6{\cdot}062 \times 10^{23}$) and k is Boltzman's constant, i.e. the gas constant for a single molecule ($= 1{\cdot}372 \times 10^{-16}$). It follows that the value of P for a gas or vapour should be given by

$$P = P_D + P_\mu$$
$$= P_D + \frac{B}{T}$$

where

$$B = \frac{4\pi N\mu^2}{9k}$$

Hence, if it is found that the value of P does not alter with temperature, then $B = 0$ and $\mu = 0$; that is, the molecule does not possess an appreciable electric moment. If it is found that P diminishes with increasing temperature, then from the slope of the P, $1/T$, curve the value of μ can be calculated. This equation has been tested for a number of gases, and is found to hold accurately. As an illustration we may consider the data in table 36 which is calculated from the measurements of Smyth and Zahn.† It will be seen that

TABLE 36

Change of Electrical Moment with Temperature

Ethane.		*Ethylene.*		*Acetylene.*			*α-Butylene.*		
T	P	T	P	T	P	T	P	P_μ	P_D
200·1	11·10	237·4	10·83	196·3	10·00	273·5	23·81	3·08	20·73
294·3	11·18	295·6	10·78	198·5	9·93	293·9	22·99	2·87	20·12
364·7	11·19	296·3	10·78	295·7	9·96	298·6	23·08	2·83	20·25
470·1	11·28	366·5	10·81	365·3	9·97	373·0	22·36	2·27	20·09
		460·9	10·73	460·5	9·96	465·7	22·02	1·81	20·21
$\mu = 0$		$\mu = 0$		$\mu = 0$		$\mu = 0{\cdot}37 \times 10^{-18}$ *e.s.u.*			

* *J. Amer. Chem. Soc.*, 1927, **49**, 1676.
† *Ibid.*, 1925, **47**, 2501.

for ethane, ethylene, and acetylene, P is practically constant; for these gases it follows that $\mu = 0$. α-Butylene shows, however, a definite fall in P as the temperature rises; the slope of the curve gives $\mu = 0{\cdot}37 \times 10^{-18}$ *e.s.u.* Using this value of μ to calculate $P\mu$ at each temperature, and subtracting from P, we get the distortion term P_D. It is interesting to note that for α-butylene, which contains four carbon atoms, this term is almost exactly twice the value found for the other three gases which contain two carbon atoms. The moment of the α-butylene molecule is small compared with that found, for example, in water, so that the orientation term is small compared with the distortion term.

The value of P in dilute solution is found to vary in a similar manner, and can also be used to calculate μ. These methods, depending upon temperature variation, have the advantage that they give values of μ and $P\mu$ which are quite independent of any assumptions about the value of P_D. The temperature variation is, however, small, and is difficult to measure with accuracy; hence another method is frequently employed to determine μ, which involves a small uncertainty, but is sufficiently accurate for most purposes. This consists of determining P for a vapour, or a dilute solution at a known temperature, and subtracting P_E calculated from the refractive index, thus obtaining $P_A + P\mu$. Since P_A is usually small, it is neglected, and $P - P_E$ is taken as $P\mu$. The error thus introduced is not large; thus, for water, $P_A = 5{\cdot}3$ and $P = 51{\cdot}0$. It is necessary to bear this approximation in mind when discussing the values found for dipole moments; a large value of μ means undoubtedly that the molecule possesses a considerable dipole, but a small value, unless it is determined by the method of temperature variation, may be due to the neglected term P_A, which represents the atomic polarisation.

Table 37 gives the electrical moments of a number of molecules obtained by these methods. It is interesting, in the first place, to compare the observed figures with the predicted value for complete separation into ions. This would correspond to charges of $e = 4{\cdot}77 \times 10^{-10}$ *e.s.u.* separated by a distance of the order of a molecular diameter, say 10^{-8} cm., thus giving $\mu = 4{\cdot}77 \times 10^{-18}$ *e.s.u.* It will be seen that this figure is only approached by the salt, silver perchlorate, and by nitrobenzene, which, as will be shown in the next chapter,

TABLE 37

Dipole Moments of Molecules

Substance.	$\mu \times 10^{-18}$ *e.s.u.*	*Conditions.*	*Observer.*
Ethane	0	Gas	S. & Z.
Ethylene	0	,,	,,
Acetylene	0	,,	,,
α-Butylene	0·37	,,	,,
Carbon tetrachloride	0	Solvent, benzene	K. & W.
Benzene	0·06	,, CCl_4	,,
Stannic iodide	0	,, benzene	A. & W.
Toluene	0·52	,, ,,	K. & W.
	0·40	,, CCl_4	,,
Hydrochloric acid	1·03	Gas	S.
Hydrobromic acid	0·79	,,	,,
Hydriodic acid	0·36	,,	,,
Water	1·98	,,	,,
Methyl alcohol	1·78	,,	,,
Ethyl alcohol	1·85	,,	,,
Phenol	1·70	Solvent, benzene	K. & W.
Ethyl ether	1·22	,, CCl_4	,,
Acetone	2·70	,, ,,	,,
Ethyl acetate	1·74	,, ,,	,,
Ammonia	1·55	Gas	S.
Dimethyl aniline	1·39	Solvent, benzene	H.
Nitrobenzene	3·75	,, ,,	,,
Silver perchlorate	4·7	,, ,,	A. & W.

References :—S. & Z., Smyth and Zahn, *J. Amer. Chem. Soc.*, 1925, **47**, 2501 ; K. & W., *ibid.*, 1927, **49**, 1684, 2414 ; A. & W., Allgeier and Williams, *ibid.*, 1927, **49**, 2420 ; S., Smyth, *ibid.*, 1924, **46**, 2151 ; H. Hφjendhal, *Nature*, 1926, **117**, 896.

contains a polar linkage between nitrogen and oxygen, thus $-\overset{+}{N}-\overset{-}{O}$. The smaller polarisations found for the other substances in the table are therefore to be attributed to a distortion of the electronic shells, and may be regarded as preliminary stages in the process of ionisation.

One of the most remarkable features of the results of such investigations is the large moment observed in compounds of oxygen. This is not due to lack of symmetry in the groups attached to the oxygen atom, for water and ether both have

a large dipole moment. It appears to indicate some lack of symmetry in the oxygen atom itself. This interesting phenomenon will probably find its ultimate explanation in the unsymmetrical distribution of the valency electrons in the 2_1 and 2_2 levels, which will produce some difference in the firmness with which they are held in the molecule. A similar behaviour is shown by compounds of nitrogen and sulphur.

The values of μ calculated from the dielectric constant give merely the magnitude of the electrical moment and do not indicate which atom carries a positive charge. In the case of compounds, which contain two groups producing dipoles, it was pointed out by Sir J. J. Thomson* that the moment of the molecule as a whole should be given by adding, as vectors, the moments of the individual dipoles. Thus, for two moments a and b, the axes of which are inclined at an angle θ, the resultant is given by

$$\mu = \sqrt{a^2 + b^2 + 2ab\cos\theta}$$

Thus, to take a particular case, two groups with equal dipoles arranged in opposite directions at opposite ends of the molecule, would cancel each other's effect and give a resultant moment of zero. Hφjendahl† has used this principle to determine the sign of the dipoles in derivatives of benzene for which the angle θ can be deduced from the structural formula. The values of a and b for different groups were obtained from the moments of the monosubstituted derivatives of benzene given below.

C_6H_5X	X =	CH_3	Br	Cl	NO_2
	μ =	0·43	1·56	1·58	3·75
	sign	−	+	+	+

The sign of the dipole in the nitro group is determined by the presence of the polar bond $-\overset{+}{N}-\overset{-}{O}$ (cf. p. 114), and is marked +, since the atom attached to the ring is positively charged. The sign of other dipoles can then be deduced from the moments of suitable disubstituted derivatives. Thus, for p-nitrotoluene the calculated moment will be 3·75 − 0·43 = 3·32 if the dipole produced by the methyl group has the same sign as that in the nitro group for $\theta = 180°$ and the two

* *Phil. Mag.*, 1923, **46**, 513.
† Loc. cit. ; cf. also Ingold, *Ann. Rep. Chem. Soc.*, 1926, **23**, 147.

dipoles act in opposition. If these dipoles have opposite signs then μ calc. $= 3{\cdot}75 + 0{\cdot}43 = 4{\cdot}18$. This is much closer to the value found for p-nitrotoluene, 4·30, so it is concluded that the dipole produced by the methyl group is opposite in sign to that of the nitro group. The signs of the dipoles produced by other substituents are determined similarly, and the signs allotted in this manner are further confirmed by the moments of the ortho and meta derivatives as is shown in table 38.

TABLE 38

Dipole Moments of Polysubstituted Benzene Derivatives

Substance.	μ *obs.*	μ *calc.*	
o-Dinitrobenzene	5·95	6·50	$a = b = 3{\cdot}75$, $\theta = 60°$
m- ,,	4·02	3·75	$a = b = 3{\cdot}75$, $\theta = 120°$
p- ,,	0·8	0·00	*zero from symmetry*
s-Tribromobenzene	0·3	0·00	,, ,,
o-Nitrotoluene	3·56	3·62	$a = 3{\cdot}75$, $b = -0{\cdot}43$, $\theta = 60°$
p- ,,	4·30	4·18	,, ,, $\theta = 180°$
o-Chloronitrobenzene	4·25	4·75	$a = 3{\cdot}75$, $b = 1{\cdot}58$, $\theta = 60°$
m- ,,	3·38	3·27	,, ,, $\theta = 120°$
p- ,,	2·52	2·17	,, ,, $\theta = 180°$
p-Bromonitrobenzene	2·69	2·19	$a = 3{\cdot}75$, $b = 1{\cdot}56$, $\theta = 180°$

The signs of the group dipoles referred to the benzene nucleus are therefore given by the series

$$\underset{\text{Negative}}{\text{Me}} > \text{H} < \text{I} < \text{Br} < \text{Cl} < \underset{\text{Positive}}{\text{NO}_2}$$

This series agrees exactly with that deduced from the effect of these groups upon substitution in the benzene ring. The dipole moments give, therefore, valuable confirmation of the electronic theories of organic chemistry which have been developed to account for a number of organic reactions.

The Physical Significance of Sharing

Although we do not know the precise disposition of the orbits of shared electrons, we can, from the properties of covalent substances, deduce a number of conditions which these orbits must fulfil. The significance of the term " shared electron " can therefore be defined somewhat strictly.

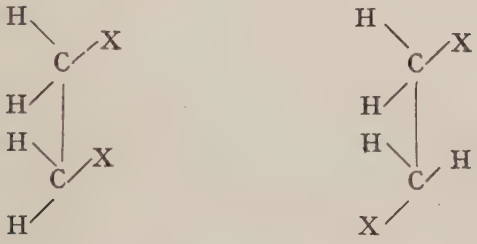
In the first place, the shared electron must play a part in the electronic structure of both of the atoms which share it, for it stabilises the structure of both atoms. In many cases this appears to be achieved by the attainment of an octet : i.e. the structure of both atoms can by means of shared electrons build up a pattern, or grouping, of its outer electrons which closely resembles that of the group of eight electrons in the inert gases. Associated with this conception of mutual sharing is the fact that, as a first approximation, the charge of the electron may be regarded as shared equally between the two atoms. It has already been noted that purely covalent substances, in particular the hydrocarbons, have very small dielectric constants, and when these are analysed are found to have zero electric moments. If the elections were shared unequally, dipoles would be produced within the molecule, and, unless these were distributed symmetrically, the molecule as a whole would have a considerable electrical moment. It is true that the dielectric constants do show the presence of dipoles, particularly in compounds containing oxygen and nitrogen ; it has already been pointed out, however (p. 104), that the magnitude of the electrical moment found for such molecules is considerably smaller than would correspond to one integral charge on adjacent atoms. To a first approximation, it is therefore permissible to sum the charges on each atom by counting each electron at half-value.* This method of calculation gives neutral atoms in all substances which contain atoms of normal valency linked by covalencies. Thus, in carbon tetrachloride, the carbon atom has a half-share in eight electrons, giving a charge of -4, and a core with a charge of $+4$. Each chlorine atom has six unshared electrons, and a half-share in two, giving a charge of -7 ; its core has a corresponding charge of $+7$. When an element exhibits higher valencies it is found that this method of calculation indicates the presence of integral charges on certain atoms, and such substances have a large electrical moment. The discussion of these cases in detail is deferred until the next chapter (p. 114).

Finally, the properties of shared electrons are intimately connected with the phenomena of stereochemistry. It is evident that a polar valency, in which the ions are separate

* Lowry, *Trans. Faraday Soc.*, 1923, **18**, 285.

entities, cannot be accepted as a picture of a directed valency linkage. We must, therefore, ascribe to the covalent link the definite space direction which renders possible stereoisomerism, optical activity, etc. It may be noted here that the covalent linkage appears to possess this important property, not only when two electrons are shared, but also when this linkage is formed by one, or three or more electrons.

The covalency linkage, composed of a shared pair of electrons, has another property which is very suggestive. This is the freedom of rotation about such bonds which is exhibited by the vast majority of organic substances. Thus, stereoisomerides of the type



do not exist, for by rotation of the halves of the molecule about the link joining the two carbon atoms, the two formulæ become identical. This free rotation about a single bond appears to imply a definite relation between the phases, and distribution in space of the orbits of a shared pair, which may be connected with the very common occurrence of duplet linkages.

During the last two years the new mathematical weapon of the wave mechanics of Schroedinger has been applied to the problem of molecular structure, and a quantum theory of valency is now being developed. It is found that the valency of an atom is largely determined by the same factor which fixes the multiplicity of its spectral terms, i.e. by the resultant spin of its electrons. In a duplet linkage it appears that there is an interchange of two electrons between levels of opposite spin quantum numbers, and that the saturation of such valency linkages is connected with the balancing of the spin of the electrons. This theory is more conveniently discussed in chapter X (p. 191) after the problems presented by higher valencies than the normal one have been dealt with.

Covalencies, Electrovalencies, and the Parachor

In the discussion of the parachor in chapter III we were concerned chiefly with organic substances containing covalent linkages. The fundamental hypothesis used in deducing the atomic parachors can therefore be translated into terms of the electronic theory by stating that the contribution to the parachor of a shared pair of electrons is zero. The significance of this hypothesis becomes clearer when parachors are analysed, not in terms of atoms and linkages, but in terms of electrons and cores.

In the first place let us consider saturated compounds in which the constituent elements exhibit their normal valency. Let the effect of the core of each atom be indicated by dashed symbols, e.g. C', H', etc., and the atomic parachors obtained in the earlier analysis be given by unmodified symbols, e.g. C, H, etc. Let y be the contribution of a shared electron, and x that of an unshared electron. To obtain the constants for carbon and hydrogen we can use, as before, the data for the paraffins, C_nH_{2n+2}. For successive members of this series we have

$$C_nH_{2n+2} \quad nC + (2n + 2)H = nC' + (2n + 2)H' + (6n + 2)y \ldots (1)$$
$$C_{n+1}H_{2n+4} \quad (n + 1)C + (2n + 4)H = (n + 1)C' + (2n + 4)H' + (6n + 8)y \ldots (2)$$

Subtracting (1) from (2)

$$C + 2H = C' + 2H' + 6y \quad \ldots\ldots\ldots\ldots\ldots (3)$$

Multiplying (3) by n and subtracting from (1)

$$2H = 2H' + 2y \quad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

and from (3) and (4)

$$C = C' + 4y \quad \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

That is, the constant for the carbon deduced by neglecting the effect of the chemical single bond, is equal to the sum of the contribution of the core + the contribution of as many shared electrons as are present, unshared, in the neutral atom. In a similar manner equations can be deduced for other atoms involving, in addition, the contribution x of unshared electrons.

$$H = H' + y \qquad O = O' + 4x + 2y$$
$$N = N' + 2x + 3y \qquad F = F' + 6x + y$$

It is evident from an inspection of these equations that the atomic parachors can only be regarded as a true measure of

the volume of the atom if the contributions of shared and unshared electrons are equal, i.e. if $x = y$. It is possible to test this hypothesis by means of certain compounds of mercury and thallium, in which the number of shared electrons varies in different series of compounds. Thus, for mercury it is highly probable that the free metal has a monatomic molecule ; hence the parachor calculated from its surface tension and density will be

$$Hg = Hg' + 2x$$

In the mercury the two electrons are shared, giving the structure shown in the adjacent formula. If R' stands for the parachor of the group R minus the contribution of a shared electron, then, as before

$R = Hg = R$

$$\begin{aligned} [P.]_{\text{obs.}} &= Hg' + 2R' + 4y \\ \Sigma[P.] &= 2R' + 2y \\ Hg = [P.]_{\text{obs.}} - \Sigma[P.] &= Hg' + 2y \end{aligned}$$

Thus the parachor for mercury obtained by subtracting $\Sigma[P.]$ from $[P.]$ obs. will equal $Hg' + 2y$. The difference between the two values will therefore give the effect of sharing upon the contribution of an electron. Similar arguments apply to compounds of monovalent and trivalent thallium, for the monovalent derivatives contain an unshared pair which is shared when the higher valency is developed. Table 39 contains data for mercury and thallium compounds which show clearly that, within the limits of experimental error, the effect of sharing an electron is zero.

TABLE 39

Effect of Shared and Unshared Electrons

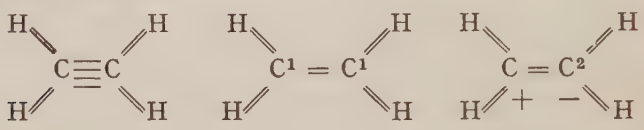
Substance.	*Formula.*	$[P.]$ *obs.*	$\Sigma[P.]$	*Atomic Parachor.*
Mercury	Hg	69·4	0	69·4
Mercury diphenyl	$Hg(C_6H_5)_2$	448·7	380·0	68·7
Thallous acetoacetic ester	$Tl(C_6H_9O_3)$	332·2	272·0*	60·2
Dimethylthallium benzoylacetone	$(CH_3)_2Tl(C_{10}H_9O_2)$	523·7	459·1*	64·6

The initial hypothesis used in deducing atomic parachors appears therefore to have a real significance, and the atomic

* See p. 145.

parachors can be taken as true measure of the atomic volume. This conclusion is supported by the periodic variation of the atomic constants with atomic number which is discussed on page 182.

We must next consider the influence of multiple bonds. Here the electronic analysis confirms the view expressed on page 41, that the large increment in parachor found for double and triple bonds is due to an interaction between the electrons which are crowded together in such linkages. For simplicity we may take the case of ethylene, which would appear to have the structure I.



I II III

The parachor obtained by summing electrons and cores is

$$\begin{aligned}[P.] &= 2C' + 4H' + 12y \\ &= 2(C' + 4y) + 4(H' + y) \\ &= 2C + 4H\end{aligned}$$

Hence, if there is no interaction between the electrons forming the multiple bond, the parachor of ethylene should be equal to the sum of the appropriate atomic constants. Actually it is 23·2 units higher than this value, so that some interaction between the electrons must be postulated. The relation between the degree of unsaturation and the parachor constant discussed on page 41 is not readily accounted for on any other hypothesis.

An alternative explanation of the unsaturation increment which has some interest, but is excluded by other evidence, can be obtained in the following manner. If ethylene has the structure II, then its parachor will be given by

$$[P.] = 2C' + 4H' + 2x + 10y$$

Also $\Sigma[P.] = 2C' + 4H' + 12y$

Subtracting

$$[P.] - \Sigma[P.] = 2(x - y)$$

Hence, the increment for the double bond could be explained if the sharing of an electron brought about a contraction of 11·6 units. The data for the mercury and thallium compounds in table 39 are quite incompatible with such a large effect, and

hence exclude this interpretation of the constant for the double bond. The structure II is highly improbable on other grounds. Thus, it contains a septet of electrons on each carbon atom, and this odd number cannot be got rid of by allotting both of the unshared electrons to one of the carbon atoms (formula III). This would produce a large dipole in the molecule, and give it a considerable electrical moment, whilst the experimental data for the dielectric constant show that its molecule has zero moment. Another objection to either formula II or III is based on stereochemical grounds, for the duplet linkage permits of free rotation about the bond between the carbon atoms. These formula are therefore incapable of accounting for the geometrical isomerism exhibited by ethylene derivatives.

The influence of a polar bond upon the parachor would appear at first sight to be readily determined by observations upon fused salts. It is found, however, that a molten salt is usually a mixture of complex ions and associated molecules, and does not consist solely of simple ions, and its parachor does not give a clear indication of the effect of a polar bond. The discussion of such systems is therefore deferred until a later chapter (p. 175). The most accurate value for the polar bond is deduced from substances which contain this linkage superimposed upon a covalency (a semipolar double bond). These are discussed in the next chapter, in which it is shown that the most probable constant for the polar bond is $-1{\cdot}6$ units. A small constant would be expected, for this linkage merely involves the transfer of an electron from one atom to another. The number of electrons is therefore unchanged when a covalency is converted into an electrovalency, and the only new factor which comes into play is the compression of the ions brought about by their mutual attraction. This can only be small, for from a variety of physical and chemical evidence it is found that atoms and ions are very incompressible, and require large forces to produce any appreciable change in the dimensions of the outer electronic orbits.

This small value for the polar bond is supported by the parachors of certain salts of organic bases, which behave in a simpler fashion than the common inorganic salts, and probably contain, in the fused state, only simple ions and undissociated molecules. These give the parachors recorded in table 73, page 177.

CHAPTER VI

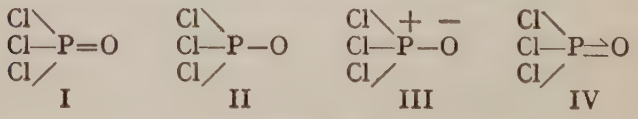
HIGHER VALENCIES

Semipolar Double Bonds

THE elements of groups V, VI, VII, and VIII of the periodic table form a number of compounds in which a valency, higher than the normal valency of $8-n$, is exhibited. One important group of these compounds, in which the higher valency is developed by the addition of an oxygen atom, can, however, be readily accounted for in terms of octets and duplets. A simple example is furnished by phosphorus oxychloride. In phosphorus trichloride one pair of electrons is unshared and can complete the octet of an oxygen atom which has only six electrons.

$$\begin{array}{c} Cl^6 \\ \| \\ Cl^6 = P^2 \\ \| \\ Cl^6 \end{array} + O^6 \longrightarrow \begin{array}{c} Cl^6 \\ \| \\ Cl^6 = P \\ \| \\ Cl^6 \end{array} = O^6$$

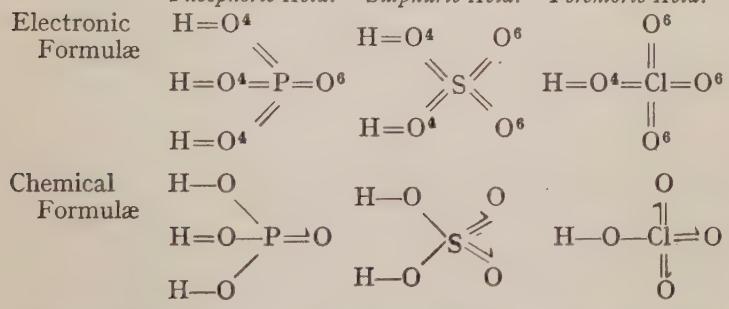
In this way Lewis accounted for a number of oxychlorides and oxyacids, but the resultant electronic formulæ differ in an important respect from the older chemical formulæ. Thus phosphorus oxychloride is usually supposed to contain pentavalent phosphorus, with a double bond between the phosphorus and oxygen atoms (I); if each duplet in the electronic formula is replaced by a chemical bond it is found that there is only one link between these two atoms. It was pointed out by Lowry* that since both of the shared electrons are supplied by the phosphorus atom there is a polar bond as well as a covalency between the two atoms. The phosphorus atom shares eight electrons, giving it a charge



I II III IV

* *Trans. Faraday Soc.*, 1923, **18**, 285.

of −4 if these are counted at half-value for each atom ; the charge on the core of the phosphorus atom is +5, giving a net charge of +1. Similarly the oxygen with six unshared and two shared electrons has a net charge of −1. The bond between phosphorus and oxygen is therefore composed of one covalency + one electrovalency and was termed by Lowry a "mixed" or "ionised" double bond. Later the writer suggested the term "semipolar" double bond, which is now commonly used. This type of linkage is conveniently represented in chemical formulæ by the symbols used in formulæ III and IV, both of which were devised by Lowry. The semipolar bond is very common in the oxyacids and their derivatives, and is also found in a number of other compounds in which other elements than oxygen can be held by a semipolar double bond. Some examples are given below.



The essential feature of this type of linkage is that one atom supplies both of the electrons which form the bond. Sidgwick* describes the atom which supplies the electrons as the *donor*, and the atom which uses them to complete its octet as the *acceptor*. He also terms the semipolar double bond the *co-ordinate link*. It is, however, by no means certain that the linkages in co-ordination compounds are invariably of this type (cf. chapter VII), so that this name does not seem to be very happily chosen.

Semipolar Double Bonds and the Parachor

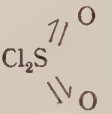
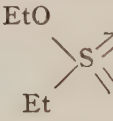
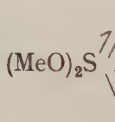
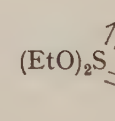
It has already been shown that the double bond found commonly in carbon compounds, in which four electrons are

* *J.C.S.*, 1923, **123**, 725.

shared between two atoms, gives a parachor increment of 23·2 units. This linkage is conveniently distinguished by the name of non-polar double bond, for it does not give rise to integral charges between the atoms. Compounds which contain a semipolar double bond are found to behave in a different manner, and the contribution of this linkage to the parachor is very small and negative. Some examples are given in table 40.

TABLE 40

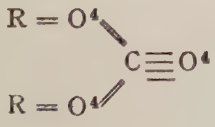
Semipolar Double Bonds

Substance.	*Formula.*	[*P.*]*obs.*	Σ[*P.*]	*Semipolar Double Bond.*
Phosphorus oxychloride	$Cl_3P \rightleftharpoons O$	217·6	220·6	−3·0
Ethyl phosphate	$(EtO)_3P \rightleftharpoons O$	399·1	403·0	−3·9
Phenyl phosphate	$(PhO)_3P \rightleftharpoons O$	686·5	687·7	−1·2
Thionyl chloride	$Cl_2S \rightleftharpoons O$	174·5	176·8	−2·3
Sulphuryl chloride		193·3	196·8	−1·65×2
Ethyl sulphite	$(EtO)_2S \rightleftharpoons O$	299·7	298·4	+1·3
Ethyl ethane sulphonate		295·8	298·4	−1·3×2
Methyl sulphate		238·9	240·4	−0·75×2
Ethyl sulphate		313·8	318·4	−2·3×2
			Mean	−1·6

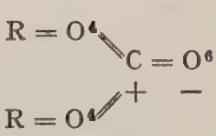
The figures in this and the following tables in this chapter unless otherwise indicated are due to Sugden, Reed, and Wilkins, *J.C.S.*, 1925, **127**, 1525. For further examples see Freiman and Sugden, *ibid.*, 1928, 263.

Here $\Sigma[P.]$ is the sum of the atomic and structural parachors except that of the linkage studied, namely, the double bond; this is obtained by subtracting $\Sigma[P.]$ from $[P.]$ obs. In all these compounds the electronic theory predicts that the double bonds must be semipolar, for, if the oxygen atoms were held by non-polar double bonds, the phosphorus or sulphur atoms would be associated with more than eight electrons. The parachor therefore supplies definite experimental evidence in favour of the electronic theory, and furthermore, gives a direct method of investigating the nature of the double bonds in other substances for which the restrictions of the octet rule are supposed by some writers to be inapplicable.

Thus, in carbonates the double bond may be of either type without exceeding the octet; if, however, the linkage is semipolar as in formula VI, the carbon atom has a shell of six electrons only. Stable shells of six can undoubtedly exist as in BCl_3 and BEt_3, so that this alternative formula cannot be



V



VI

excluded without further evidence. The parachors of alkyl and aryl carbonates show conclusively, however, that the first formula, V, is correct, and that carbon in these compounds possesses the normal octet (table 41).

TABLE 41

Carbonic Esters

Substance.	$[P.]$ *obs.*	$[P.]$ *calc. Non-polar.*	$[P.]$ *calc. Semipolar.*
Ethyl carbonate .	277·4	278·2	253·4
Phenyl carbonate .	467·4	468·2	443·4

Both kinds of linkage are found in compounds of nitrogen. Esters of nitrous acid and nitroso compounds may possess either a semipolar double bond with six electrons associated with the nitrogen atom (formula VII), or a non-polar double

bond with a completed octet (formula VIII). The parachors of substances belonging to these classes are recorded in

VII $R = N^2 = O^6$ (+ —) $\qquad R = N^2 \equiv O^4$ VIII

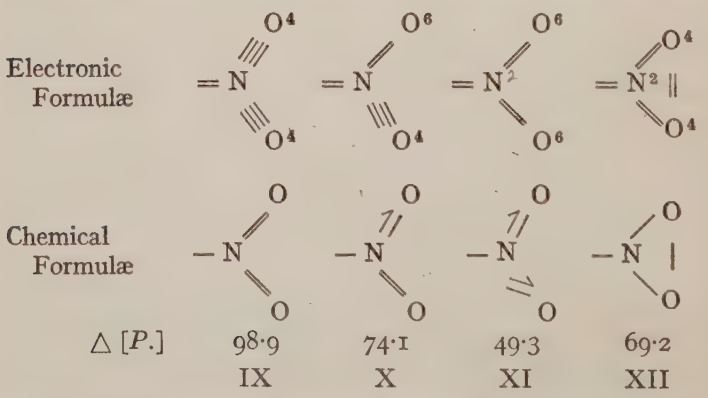
table 42. It is evident that the double bonds in these compounds are non-polar, and that in this group also the octet is attained.

TABLE 42

Nitroso-compounds and Nitrites

Substance.	[*P.*] *obs.*	[*P.*] *calc. Non-polar.*	[*P.*] *calc. Semipolar.*
Nitrosyl chloride . .	108·1	110·0	85·2
Dimethyl nitrosamine .	183·8	180·4	155·6
Diethyl nitrosamine .	260·3	258·4	233·6
n-Butyl nitrite . .	251·8	248·8	224·0
i-Amyl nitrite. . .	287·4	287·8	263·0

For the nitro group four formulæ are possible, which are set out below together with the contribution, $\triangle$ [*P.*], which the NO_2 group would be expected to give to the parachor if it had the structure indicated. Formulæ X and XII are



in accordance with the octet rule, whilst the others assume the existence of shells of ten and six electrons respectively. The parachors of a number of nitro-compounds are given in table 43, and lead to a value for the NO_2 group of 73·0 which

TABLE 43

Nitro-compounds

Substance.	[*P.*] *obs.*	Σ[*P.*]	*Nitro Group.*
Nitrogen peroxide . .	144·4	0	72·2
Nitromethane . . .	132·0	56·1	75·9
Ethyl nitrate . . .	189·6	115·1	74·5
Nitrobenzene . . .	264·5	190·0	74·5
o-Nitrotoluene . . .	301·1	229·0	72·1
m-Nitrotoluene . . .	300·6	229·0	71·6
p-Nitrotoluene . . .	302·8	229·0	73·8
o-Chloronitrobenzene . .	299·9	227·2	72·7
m-Chloronitrobenzene . .	298·9	227·2	71·7
p-Chloronitrobenzene . .	300·0	227·2	72·8
o-Bromonitrobenzene . .	312·9	240·9	72·0
m-Bromonitrobenzene . .	313·5	240·9	72·6
p-Bromonitrobenzene . .	313·5	240·9	72·6
		Mean	73·0

agrees well with formula X, in which one oxygen atom is held by a non-polar double bond whilst the other forms part of a semipolar linkage.

A similar arrangement composed of a double bond of each type is found in azoxy-compounds, and in the N-ethers of oximes which have the structures shown below.

$$-N=N- \qquad\qquad >C=N-$$
$$\quad\downarrow\!\!\uparrow \qquad\qquad\qquad\quad\downarrow\!\!\uparrow$$
$$\quad O \qquad\qquad\qquad\quad O$$

TABLE 44

Azoxy-compounds, etc.

Substance	[*P.*] *obs.*	[*P.*] *calc.*
Azoxybenzene . . .	444·7	446·6
o-Azoxytoluene . .	528·6	524·6
N-Methyl ether of benzantialdoxime .	325·9	321·1

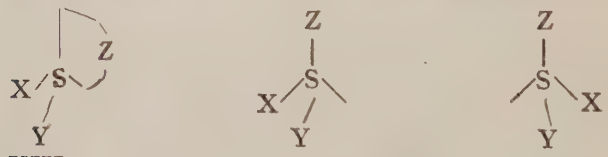
If both double bonds were non-polar the parachors would be 24·8 units higher, and if two semipolar double bonds were present the value of [*P.*] calc. would be 24·8 units less.

All the nitrogen compounds examined are in agreement

with the general rule that the fifth valency of nitrogen is always an electrovalency. This is evident in ammonium chloride, when the chlorine atom is free and ionises in solution ; the parachors show, however, that the same rule holds when the higher valencies of nitrogen are satisfied by an oxygen atom, when the polar valency forms part of a double bond. Similar rules can be formulated for the higher valencies of sulphur, but all these rules are included in, and are a necessary consequence of, the rule of eight, which limits the number of valency electrons associated with a particular atom. The maximum number of covalencies is therefore four, and the number of polar valencies which accompany them is one for pentavalent nitrogen or phosphorus, two for hexavalent sulphur, and three for heptavalent chlorine in the perchlorates, etc. The chief theoretical significance of the regularities found in the parachors of these substances, therefore, lies in the fact that these regularities provide definite experimental evidence for the validity of the octet rule.

Stereochemical Evidence for Semipolar Double Bonds

The parachor evidence is very convincingly supported in the case of compounds of sulphur by two independent types of stereochemical evidence. Substances which contain the grouping $XY.S \rightleftharpoons Z$ have in several cases been found to exhibit optical activity. If the sulphur is assumed to have a tetrahedral structure, then the group may be linked by a non-polar double bond as in XIII or by a semipolar double bond



XIII XIV

as in XIV. In the first case the molecule has a plane of symmetry through XYS and bisecting Z, whilst the semipolar structure indicates that the groups X, Y, and Z are not in the same plane as the sulphur atom, so that the molecule can exist in enantiomorphous forms. The resolution of a number of sulphur compounds containing this grouping is therefore convincing evidence that the double bond in these

compounds is of semipolar type. The first example of the optical activity of sulphur compounds, due to semipolar double bonds, was given by Phillips* by the resolution of esters of p-tolyl sulphinic acid. Later Harrison, Kenyon, and Phillips† resolved two sulphoxides, and Clarke, Kenyon, and Phillips‡ resolved a sulphonylimine in which the semipolar double bond is formed between a nitrogen atom and sulphur. The rotations found for these substances are given in table 45.

TABLE 45

Optical Activity of Sulphur Compounds due to Semipolar Double Bonds

Substance.	*Formula.*	$[\alpha]_{5461}$ *in alcohol.*	
Ethyl p-toluenesulphinate	C_7H_7, $S\rightleftharpoons O$, $Et{\cdot}O$	+ 16·52°	− 6·72°
n-Butyl p-toluenesulphinate	C_7H_7, $S\rightleftharpoons O$, BuO	—	− 3·46°
m-Carboxyphenylmethyl-sulphoxide	CH_2, $S\rightleftharpoons O$, $COOH{\cdot}C_6H_4$	+ 137°	−133·5°
4′-Amino-4-methyldiphenyl-sulphoxide	$NH_2{\cdot}C_6H_4$, $S\rightleftharpoons O$, $CH_3{\cdot}C_6H_4$	+ 123°	− 122°
m-Carboxyphenylmethyl-sulphine-p-toluene-sulphonylimine	CH_2, $S\rightleftharpoons N{-}SO_2{\cdot}C_7H_7$, $COOH{\cdot}C_6H_4$	+ 338°	− 338°

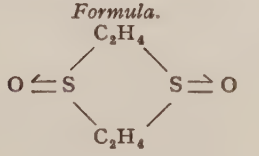
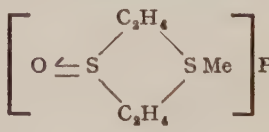
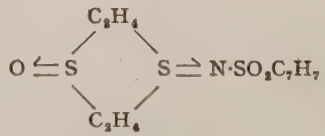
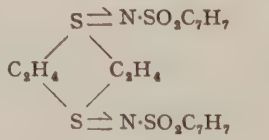
* *J.C.S.*, 1925, **127**, 2552. † *Ibid.*, 1926, 2079. ‡ *Ibid.*, 1927, 188.

Oxidation of the sulphinic esters to sulphonates and of sulphoxides to sulphones immediately destroyed the optical activity. This is to be expected, since the products contain two oxygen atoms attached to sulphur by semipolar double bonds, thus producing a plane of symmetry in the molecule.

If the atom held by a semipolar linkage in such compounds is not in the same plane as the sulphur atom and the groups X and Y, then substances containing two of these groups should exhibit geometrical isomerism and be capable of isolation in *cis* and *trans* inactive modifications. This has been realised experimentally by Bell and Bennett,* who have prepared several pairs of isomerides of this type, which are differentiated by means of their melting points and crystalline form (table 46).

TABLE 46

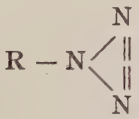
Geometrical Isomerism due to Semipolar Double Bonds

Substance.	*Formula.*	*α form. M.p.*	*β form. M.p.*
Dithiandioxide		263° dec.	235°–250° dec.
Dimethylethylene-disulphoxide		163°–164°	128°–130°
Dithianmonoxide methylsulphinium picrate		187°	137°
Dithianmonoxide S-p-toluene sulphonylimine		230°–234°	176°–177°
Dithian di-S-p-toluene sulphonylimine		250°–255° dec.	200°–210° dec.

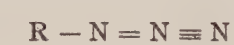
* *J.C.S.*, 1927, 1798; 1928, 86.

The Structure of Azoimides

Another group of substances, in which the octet rule sets a limit to the formulæ based on the older theories of valency, is furnished by the azoimides. The group of three nitrogen atoms in these substances is usually assigned a ring structure as in XV, or an open chain arrangement as in XVI. When

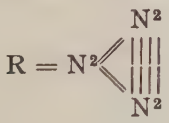


XV



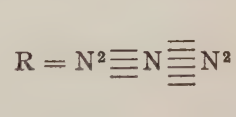
XVI

these are translated into electronic formulæ it is evident that XVI is incompatible with the octet rule, for the central nitrogen atom is associated with ten electrons (XVIII). Alternative open chain formulæ XIX and XX can be written which assign an octet to each atom.



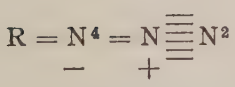
Δ [P.] = 77·4 for N_3

XVII



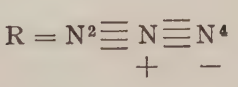
Δ [P.] = 107·3

XVIII



Δ [P.] = 82·5

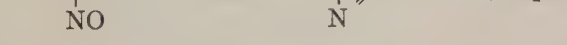
XIX



Δ [P.] = 82·3

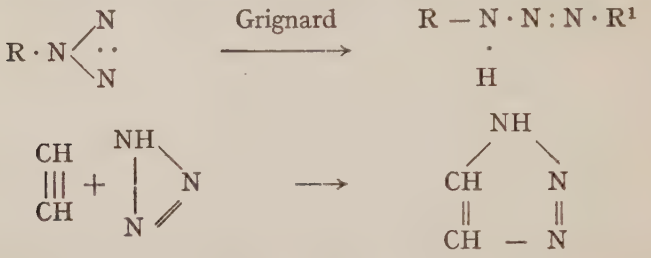
XX

The ring formula was originally proposed by Curtius,* and accounts satisfactorily for the formation of azoimides by the elimination of water from nitrosohydrazines.



* *Ber.*, 1890, **23**, 3023.

This formula was criticised by Thiele* on the following grounds. The azoimides readily form diazoamino-compounds with Grignard reagents, and osotriazoles with acetylene derivatives. These reactions are readily accounted for by an open chain



formula, but on the ring formula involve the breaking of a single bond, whilst a double bond remains intact. Since it is now known that these substances readily rearrange to give tautomerides, this argument is not conclusive.

The molecular refractions and dispersions of a number of triazo-compounds have been measured by J. C. Philip,† and the contribution of the N_3 group is found to be 8·90. This is larger than the value for three nitrogen atoms (3 × 2·48), and Philip, reviewing the available evidence, came to the conclusion that the cyclic formula was the most probable.

The parachors of a number of azoimides have recently been determined by H. Lindemann and H. Thiele,‡ with the results shown in table 47.

TABLE 47

Azoimides

Substance.	*Formula.*	[*P.*] *obs.*	Σ[*P.*]	N_3
Triazoacetic ester	$N_3 \cdot CH_2 \cdot CO_2Et$	277·0	198·9	78·1
Triazoacetone	$CH_3 \cdot CO \cdot CH_2 \cdot N_3$	220·9	143·1	77·8
Phenyl azoimide	$C_6H_5 \cdot N_3$	267·3	190·0	77·3
o-Toluyl azoimide	$C_7H_7N_3$	303·8	229·0	74·8
p-Toluyl azoimide	$C_7H_7N_3$	307·0	229·0	78·0
			Mean	77·2

The mean value found for the parachor of the N_3 group is 77·2; this should be compared with the predicted values

* *Ber.*, 1911, **44**, 2524. † *J.C.S.*, 1908, **93**, 918; 1912, **101**, 1866.
‡ *Ber.*, 1928, 1529.

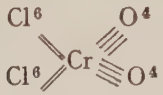
given under the formulæ. It is evident that the parachors can only be accounted for by the cyclic formulæ XVII. Formula XVIII, which violates the octet rule, is definitely excluded, and the alternative open chain formulæ XIX and XX also predict a parachor which is markedly higher than the experimental figure. Formula XX is of some interest, since it contains a polar bond superimposed upon a non-polar double bond; this is termed by Lindemann and Thiele "a one-third polar triple bond."

Validity of the Octet Rule for Other Elements

The rule that eight is the maximum number of valency electrons which can be associated with an atom in stable compounds was limited by Lewis, and also by Langmuir, to the elements of the first period of Mendeléef's table. It appears very probable, however, from the experiments discussed in the earlier sections of this chapter, that a number of compounds of phosphorus and sulphur, elements of the second period, possess structures in which the octet rule is obeyed. It should be noted that if these elements could form stable shells with a larger number of electrons, then the electrostatic field of the semipolar double bond would tend to produce this further sharing. Thus the positively charged phosphorus atom in phosphorus oxychloride must undoubtedly attract the unshared electrons of the oxygen atom, and, but for the limit set by the octet rule, the molecule would tend to "close up" and eliminate the electrical dipole by the formation of a non-polar double bond. The occurrence of so many semipolar double bonds in compounds of these two elements indicates that the atoms of phosphorus and sulphur offer a considerable resistance to any attempt to produce an external shell containing more than eight electrons.

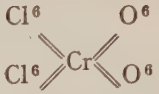
Similar evidence is available for a number of other elements of higher atomic number. Thus the parachor of chromyl chloride is found to be 199·1. No other data are available for fixing the parachor of chromium, for this element does not form fusible covalent compounds in which it exerts its normal valency. It is probable from the general trend of the curve of atomic parachors with atomic number, that chromium must have a parachor lying between 40 and 60 units. If chromyl chloride is supposed to have the structure XXI, in which the oxygen atoms are held by non-polar double bonds, then the

value for the parachor of chromium deduced from this substance is 4·1, which is far too small. If, however, the double



Cr = 4·1

XXI



Cr = 53·7

XXII

bonds are semipolar, then the value Cr = 53·7 is obtained, in much better agreement with the expected figure. A similar result is found from the data for potassium dichromate, which on the hypothesis of semipolar double bonds gives a rough value of about 54 units for chromium. The octet rule seems, therefore, to hold for chromyl chloride, as indeed would be expected from the close chemical resemblance between hexavalent chromium and hexavalent sulphur. It is noteworthy that this value for chromium refers to the hexavalent element with the electronic configuration 2.8.8.6; whilst trivalent chromium, with the configuration 2.8.11.3, gives nearly the same value in its co-ordination compounds.

For selenium direct evidence for the existence of semipolar double bonds has recently been obtained.* The parachor of this element, from the five compounds listed in table 48, is found to be 62·5.

TABLE 48

Parachor of Selenium

Substance.	[*P.*] *obs.*	Σ[*P.*]	*Se.*
Diphenyl selenide . . .	445·6	380·0	65·6
Diphenyl diselenide . .	506·5	380·0	63·2 × 2
Phenyl selenium bromide .	321·4	258·0	63·4
p-Chlorophenylselenocyanate .	349·3	291·1	58·2
p-Bromophenylselenocyanate .	366·1	304·6	61·5
		Mean	62·5

In these compounds selenium exerts its normal valency of two; in phenyl selenium oxide, phenyl selenious acid, and selenium oxychloride, the valency of four is reached. If the octet rule holds for this element, the oxygen atoms must be held by semipolar double bonds. The parachors of these

* Henley and Sugden, *J.C.S.*, 1929.

substances are given in table 49, and it will be seen that the presence of a non-polar double bond in the molecule cannot be admitted. Phenyl selenious acid gives a lower parachor than that calculated even for a semipolar double bond, but this is only to be expected, for this substance contains a free hydroxyl group and will therefore give an associated liquid with a low parachor. Selenium oxychloride behaves similarly, and in many of its physical properties shows a close resemblance to the typical associated liquids. Thus it has a high dielectric constant, and its molecular weight in benzene indicates association. It is evident from the results that the octet rule holds

TABLE 49

Semipolar Double Bonds in Selenium Compounds

Substance.	*Formula.*	[*P.*]*obs.*	[*P.*]*calc. Semi-polar.*	[*P.*]*calc. Non-polar.*
Diphenyl selenium oxide	$Ph_2Se \rightleftharpoons O$	461·6	460·9	485·7
Phenyl selenious acid	$PhHOSe \rightleftharpoons O$	299·5	308·0	332·8
Selenium oxychloride	$Cl_2Se \rightleftharpoons O$	181·1	189·5	214·3

for these compounds of selenium at least, and in spite of the electrical influences set up by the polar bonds, an outer shell containing more than eight electrons is not attained.

Measurements of the surface tension of osmium tetroxide have been made by von Wartenburg,* and provide a test of the validity of the octet rule for an element of high atomic number. The parachor calculated from these observations is 154·0; if the double bonds holding the four oxygen atoms are semi-polar, this gives a parachor for osmium of 154·0 − 73·6 = 80·4, whilst the assumption of non-polar double bonds gives a value

* *Annalen*, 1924, **440**, 97.

of 154·0 − 172·8 = − 18·8. Although no direct evidence is available from other osmium compounds, the general trend of the atomic number — parachor curve (p. 183) indicates that all the elements in this transition series from tungsten to lead have parachors lying between 50 and 90 units. The value Hg = 69 has been well established by observations on the metal and on its aryl derivatives, so that the first figure for osmium, 80·4, is the only reasonable one to accept. This, of course, indicates that in osmium tetroxide the osmium atom has an outer shell of eight electrons, and is further evidence for the general validity of the octet rule. In every case which has yet been examined in which a surplus of electrons above eight would be indicated by the conversion of a semipolar double bond into a non-polar linkage, the parachor shows that the rule of eight holds good for elements of high atomic number as well as those in the first period of Mendeléef's table.

Higher Halides

The higher valencies exhibited by elements in the latter half of the periodic table are thus accounted for satisfactorily when these valencies are used to hold divalent elements, e.g. oxygen. In such substances the electronic formulæ involve only the duplet linkage or multiples of it, and the number of duplet linkages on each atom is limited by the octet rule. When, however, compounds of the type of PCl_5, SF_6, etc., are considered, it is evident that the rule of eight must be abandoned or else the existence of linkages composed of one shared electron must be admitted, for in these substances more than four atoms or groups appear to be attached to the central atom. It is possible, of course, to formulate these higher halides as polar compounds as suggested by Langmuir* (formula XXIII), but the general properties of many of these higher valent compounds do not lend any support to this view. They are usually volatile substances and are readily soluble in

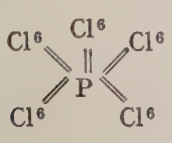
XXIII

* *J. Amer. Chem. Soc.*, 1919, **41**, 919.

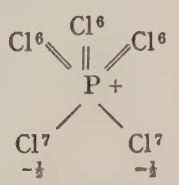
organic solvents, whilst those which can be examined in the pure liquid state do not exhibit an appreciable electrical conductivity. A small conductivity has been found for PCl_5 dissolved in nitrobenzene, but transport measurements show that the phosphorus moves to the anode* so that the ions are probably formed by combination with the solvent. A similar interpretation may also be given to Plotnikov's observations of the conductivity of PBr_5 dissolved in bromine. In dilute solutions the conductivity is small, but in strong solutions is large, whilst at intermediate concentrations two liquid layers are formed.

Antimony pentachloride, which can be readily handled in the liquid state, is clearly a non-polar compound. Its conductivity is negligibly small, and its dielectric constant is low (3·78) ; it melts at — 6° and boils at 140°, and is miscible with benzene, ether, and chloroform,† so that it cannot be regarded as a polar compound.

If, however, these substances are formulated as covalent compounds, it is necessary to abandon the limit of eight external electrons set by the octet rule, or else to assume that some of the linkages are composed of one shared electron (formulæ XXIV and XXV). The first formula is that adopted by Lewis‡ and by Sidgwick,§ whilst the second formula was



XXIV



XXV

put forward by Prideaux.‖

The one electron linkage, which is conveniently termed a singlet link, played an important part in the earlier electronic theories of Stark,¶ and was used by Thomson** to formulate

* Holroyd, *J.C.S.*, 1925, **127**, 2492.
† Abegg, Vol. III, Part 3, p. 613.
‡ *Valence and the Structure of Atoms and Molecules*, 1923, p. 101.
§ *The Electronic Theory of Valency*, 1927, 130.
‖ *Chem. and Ind.*, 1923, **42**, 672.
¶ *Atomdynamik*, Hirzel, Leipzig, 1916.
** *Phil. Mag.*, 1921, **41**, 510.

the hypothetical compound NCl_5. More recently Prideaux's formula for phosphorus pentachloride has been applied by Ingold and Ingold* to explain certain cases of substitution in aromatic compounds. Some years earlier, Robinson,† and Kermack and Robinson,‡ used singlet linkages to represent unstable intermediate phases in a number of organic reactions, e.g. the Wagner–Meerwein transformation and the trans Beckmann change.

The conception of singlet linkages has been criticised mainly on the ground that such linkages must be very unstable. This criticism does not appear to the writer to be well founded. We are still very ignorant of the conditions which determine the stability of a molecule, and it is evident from a comparison of a few simple substances that chemical stability depends chiefly upon the nature of the atoms which take part in a linkage, and only to a smaller extent upon the nature of the link itself. Thus the chlorides of the adjacent elements carbon and nitrogen differ enormously in stability, yet in both cases the link is probably a duplet. On the other hand, B_2H_6, in which the presence of singlet linkages must be admitted, is moderately stable and is prepared by heating B_4H_{10} to 100° C. A better comparison can be made between the stability of singlet and duplet linkages when they join the same type of atom in the same molecule. If the Prideaux formula is accepted for PCl_5, this substance gives the necessary conditions for making the comparison. As would be expected, the chlorine atoms held by singlets are rather less firmly bound, and on heating the substance dissociates into PCl_3 and Cl_2. The difference in stability between singlet and duplet linkages is not, however, large, for the degree of dissociation in the vapour state (which by increase of volume favours dissociation) is less than 50% at 200°.

The alternative hypothesis of an extended valency shell of more than eight electrons is definitely opposed by the parachor evidence discussed in the preceding sections of this chapter. So far as the occurrence of double bonds is concerned the limits set by the octet rule predict in every case the number of semi-polar double bonds found in the molecule. If, for example, sulphur has an outer shell of twelve electrons in SF_6, it is difficult to

* *J.C.S.*, 1926, 1315.
† *Mem. Manchester Lit. and Phil. Soc.*, 1920, lxiv, No. 4.
‡ *J.C.S.*, 1922, **121**, 416.

understand why this shell is not attained in sulphuryl chloride and esters of sulphuric acid, etc. Further general arguments against stable shells of more than eight electrons can be inferred from the stable groups found in the structure of atoms. The next highest stable group to the octet is a shell of eighteen electrons, but this does not begin to form until some electrons are bound in orbits of higher quantum number, and is apparently not stable as an outermost shell. If higher valencies are due to the formation of this group by means of duplet links, the highest valency found should be nine. The highest valency known is, of course, eight, e.g. OsF_8, $[MoCy_8]''''$, and this follows at once from the octet rule in which the limiting number of atoms which can be attached to a nuclear atom by singlet linkages is eight. If the fluorine atoms in OsF_8 were held by duplet links, this molecule would contain a shell of 16 electrons, and by analogy with similar compounds in which the group of eight is nearly attained, one would expect a ready formation of complex ions with a co-ordination number of nine, e.g. $H[OsF_9]$.

Singlet Linkages and the Parachor

The probable contribution to the parachor of a singlet linkage can be inferred from the relationship between the parachor constant and the number of electrons which form a bond (table 50). The duplet linkage, or the chemical single bond, is chosen arbitrarily as zero (cf. p. 37), and therefore represents only a reference level from which the effect of other structures is measured. In the non-polar double and triple bonds each

TABLE 50

Number of Electrons and Structural Constants

Linkage.	*No. of Electrons.*	*Parachor.*
Triple bond	6	46·6
Non-polar double bond	4	23·2
Single bond (duplet)	2	0·0
Singlet	1	— 11·6
Semipolar double bond	2	— 1·6
Semipolar single bond	1	— 12·4

electron in excess of two adds 11·6 units to the parachor; it seems highly probable, therefore, that the singlet link, with

one electron less than the duplet link, will cause a diminution of the parachor of 11·6 units. A small correction is required when the singlet is associated with a polar bond as in PCl_5. If each shared electron is counted at half-value, then it is found that the phosphorus atom carries a positive charge, as in $POCl_3$, and that each chlorine atom carries a half-negative charge. (This half-charge does not, of course, mean a splitting of the electron, but indicates that the shared electron, if equally shared, is for half of its time of revolution in its orbit associated with the chlorine atom.) The effect of the electrical dipole associated with the singlet link will obviously be half of the value found for the semipolar double bond, namely, $\frac{1}{2} \times (-1{\cdot}6) = -0{\cdot}8$. The constant for a charged singlet link, termed by Ingold and Ingold* a semipolar single bond, will therefore be — 12·4.

The alternative formula XXIV (p. 129) contains a shell of ten electrons, and it is less easy to predict the effect of this structure upon the parachor. It involves a certain crowding of electrons about the central phosphorus atom, which, by analogy with the effect of crowding in ring structures and multiple bonds (p. 41), might give a small increase in the parachor. Since in formula XXIV two electrons above the normal number are shared by six atoms, the effect should be about $\frac{1}{3}$ of the increment found for a double bond in which two extra electrons are shared by two atoms. The parachor increment for the duplet formula is therefore assumed to be $23{\cdot}2/3 = +7{\cdot}7$.

The observed and calculated values of the parachors of certain higher halides are compared in table 51. In each case it will be seen that the experimental figures are in good

TABLE 51

Singlet Linkages in Higher Halides

Substance.	*Formula.*	[*P.*] *obs.*	[*P.*] *calc.* *Singlets.*	*Duplets.*
Phosphorus pentachloride	PCl_5	282·5	284·4	316·9
Antimony pentachloride	$SbCl_5$	311·8	312·7	345·2
Monohydrate of selenium oxychloride	$Cl_2Se(OH)_2$	222·8	220·5	253·0

* Loc. cit.

agreement with the singlet formula, and indicate clearly that the octet rule is not violated even in the higher valencies of these elements. This is also true for the monohydrate of selenium oxychloride, which has probably the structure $Se(OH)_2Cl_2$, and should, therefore, contain two singlet links.

It should be noted here that an alternative interpretation of the parachors of these substances is possible, which would reconcile these results with the duplet formula XXIV. If this formula is examined it will be seen that the molecule contains ten shared electrons, whilst the normal number shared when a phosphorus atom and five chlorine atoms exert their normal valencies is eight. If it is assumed that *the sharing of an electron produces a contraction of* 11·6 *units*, then, whilst the sharing of eight is allowed for in computing the atomic constants, the sharing of the extra two electrons will give a decrement of 23·2 units, which is very nearly the same as that predicted for the singlet formula. In a similar manner the decrements found for the metallic derivatives of β-diketones, discussed in the next chapter, can all be accounted for without using singlet linkages.

This hypothesis has already been discussed in connexion with the determination of atomic parachors (p. 111), and, in the author's opinion, is clearly excluded by the data for mercury and thallium compounds which are there quoted. The adoption of this hypothesis also leads to structures for the non-polar double and triple bonds which are difficult to reconcile with their stereochemical properties and cannot be made to account for the relation between the parachor increments for these structures and those for closed rings (p. 41). A further argument against this hypothesis is furnished by the improbable distribution of polarities within the molecule which is found in the duplet formulæ for metallic derivatives of β-diketones (p. 142). For these reasons the hypothesis of singlet linkages is adopted throughout the remainder of this book, since it gives a consistent interpretation of nearly all the parachor anomalies which have so far been encountered.

The Extended Electronic Theory of Valency

From the evidence discussed in the preceding section it seems highly probable that the octet rule sets a limit to the valency shell of all atoms, and, as a necessary corollary, linkages composed of an odd number of electrons must be

recognised. By using such linkages it is possible to give a formal representation of the structure of many substances which are not readily accounted for by the older theory. Such formulæ are not merely speculative, but can be tested experimentally by determinations of the parachor and other physical properties, e.g. electrical conductivity, etc.

Rules for constructing such electronic formulæ may be defined as follows :—

(1) The number of electrons associated with each atom in the molecule does not exceed eight.

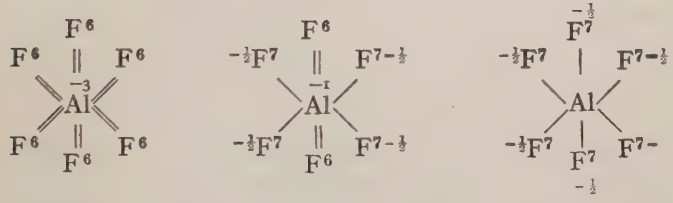
(2) Atoms may share 1, 2, 3, 4, 5, or 6 electrons with another atom.

The first rule is obviously the octet rule of Lewis, but is now considered to apply to all atoms. The second rule abandons the restriction that shared linkages must be duplets, or multiples of duplets, and permits the use of an odd number of electrons to form a covalency. It is evident that all the higher halides can be formulated simply in accordance with these rules ; the limit is reached with OsF_8, in which eight fluorine atoms are supposed to be held by eight singlet linkages.

These rules alone are not, however, sufficient to define completely the formula of many substances, and alternative formulæ can often be written using different arrangements of singlet linkages. It is therefore important to seek for some guiding principle by which a selection can be made between alternative formulæ in those cases in which experimental evidence is not available. Such a guide is found in the distribution of polarities within the molecule. Since atoms and molecules are assemblages of electrically charged particles, it would be expected that the greatest stability would be reached when all the atoms in the molecule had become neutral by sharing a sufficient number of electrons. This complete neutralisation of intramolecular charges is limited by the octet rule, and integral dipoles are certainly found in compounds containing semipolar double bonds. At the other end of the scale, elements possessing a small number of valency electrons can lose these to give polar compounds, e.g. NaCl. In both series of compounds the sign of the charge is determined by the specific properties of the atoms concerned, and can be ascribed to their varying attraction or affinity for electrons. Thus, metallic atoms have only a small electron affinity and tend

to become positively charged whilst the halogens and oxygen have a large electron affinity and can assume a negative charge. These characteristic properties of the elements must also be expected to hold in compounds containing singlet linkages, and a limit is thus set to the electronic formulæ which may be used to represent a particular substance.

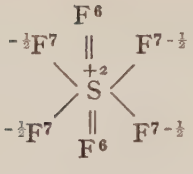
This point may be illustrated by reference to the structure of the ion AlF_6 found in cryolite, for which the three following formulæ may be written. In XXVI the octet rule is violated, and a shell of twelve electrons is associated with the aluminium



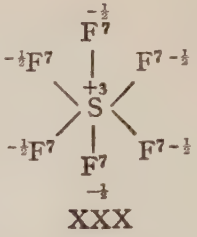
XXVI XXVII XXVIII

atom, giving it a net charge of -3. It is thus negative to the fluorine atoms, and the molecule possesses a distribution of polarities in the opposite sense to that which would be expected from the usual electrochemical properties of these elements. Since fluorine has a great affinity for electrons, we may suppose that four of these atoms in XXVI attract an electron so strongly that it ceases to be shared by the aluminium atom, thus giving the four singlet linkages in XXVII. Here the octet rule is obeyed, but the aluminium atom still retains a residual negative charge. In XXVIII the remaining fluorine atoms have acquired the sole interest in an electron ; the metal atom is neutral and the negative charge of the ion is distributed evenly over the halogen atoms. This formula seems, therefore, to be the best representation of the structure of the cryolite ion. At present no measurements have been made of the parachor of this substance, but a very similar arrangement of six singlet linkages is found in aluminium acetylacetonate (p. 147).

Another example is furnished by sulphur hexafluoride, for which the four following formulæ may be written.

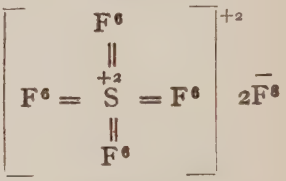


XXIX



XXX

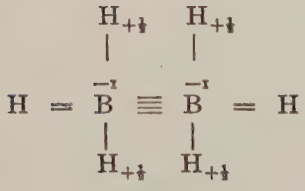
XXXI



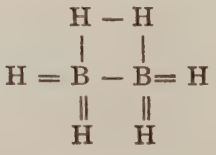
XXXII

In XXIX and XXX the sulphur atom is positively charged, and the fluorine atoms held by singlets are negative; this arrangement of polarities is, of course, in agreement with the characters of these two elements. Formula XXXI, on the other hand, contains only neutral atoms because of the different arrangement of the singlet linkages. The third formula represents that of a salt, and it may be noted that in general every formula containing singlet linkages can be replaced by an alternative polar formula. Since SF_6 is a gas, and is chemically inert, the polar formula is definitely excluded; the parachor would serve to distinguish between XXIX, XXX, and XXXI, but so far the surface tension of this substance has not been determined.

Finally, it is possible by means of singlet linkages to write structural formulæ for the boron hydrides. Thus, for diborane, B_2H_6, the structures XXXIII and XXXIV are possible.



XXXIII



XXXIV

In XXXIII, which was independently suggested by Main Smith* from the reactions of this substance, the boron atoms have completed an octet, but carry a negative charge, whilst four of the hydrogen atoms are positive. In XXXIV the boron atoms have an outer shell of six, and all the atoms in the molecule are neutral. Here again the parachor will distinguish between the two formulæ; for XXXIII, [*P.*] *calc.* = 108·6, and for XXXIV, [*P.*] *calc.* = 86·4, so that a determination of the surface tension of diborane would be of considerable interest.

* *Chem. News*, 1927, **135**, 81.

CHAPTER VII

APPLICATIONS OF THE THEORY OF ODD ELECTRON LINKAGES

Co-ordination Compounds

A SATISFACTORY theory of valency must not only be capable of accounting for the simpler inorganic compounds, but must also include within its scope the complex compounds which are usually formulated by Werner's theory of co-ordination. In these substances the ordinary rules of valency seem to be disregarded, and the stability apparently depends upon the distribution of a definite number of groups or atoms about a central atom. The assemblage thus produced may be neutral, or may carry a positive or negative charge; in the latter case it constitutes a complex ion, and an appropriate number of ions of the opposite sign will be found in the molecule. Werner writes the complex ion within a square bracket, thus, $[Co(NH_3)_6]Cl_3$, to differentiate between the groups or atoms which ionise and those which are attached to the central atom. The latter are described as groups in the co-ordination zone, and the number of such groups attached to the central atom is termed the co-ordination number. This number may have any value from 1 to 8; some examples are given below, including both covalent and ionised substances.

Co-ordination Number.	1	2	3	4
Covalent substances	$[HCl]$	$[SH_2]$	$[BCl_3]$	$[CCl_4]$
Ionised substances	$[Fe(NO)]SO_4$	$[Ag(CN)_2]K$	$[Ag(NH_3)_3]Cl$	$[BF_4]K$

Co-ordination Number.	5	6	7	8
Covalent substances	$[PCl_5]$	$[SF_6]$	—	$[OsF_8]$
Ionised substances	$[HgCl_5]Cs_2$	$[Co(NH_3)_6]Cl_3$	$[SiF_7](NH_4)_3$	$[Mo(CN)_8]K$

For covalent substances the co-ordination number is determined by the ordinary rules of valency, but in the complex ions this is no longer true. Here there is a well-marked tendency to form complexes with co-ordination numbers of 4, 6, or 8, whatever the normal valency of the central atom, and ions with odd co-ordination numbers are only rarely found.

Sidgwick* has shown that the maximum co-ordination number of an atom is determined by its position in the periodic table, and is 2 for hydrogen, 4 for the elements of the first short period (Li — F), 6 for the second and third periods (Na — Br), and 8 for elements from rubidium onwards. This rule is true for practically all the co-ordination compounds whose constitutions have been accurately determined, but its physical basis is at present obscure. It was originally correlated with Bohr's symmetrical subdivision of the electrons in the principal quantum levels which gave the scheme 2, 4.4, 6.6.6, 8.8.8.8, for the numbers of electrons in the sub-groups of the K, L, M, and N levels. This distribution is now abandoned, and the sub-groups are known to have the following numbers of electrons, 2, 2.6, 2.6.10, 2.6.10.14 (cf. p. 70); it is not easy to trace any simple relation between these numbers and the rule which undoubtedly fixes the maximum co-ordination number.

It will be noted that neutral molecules, e.g. NH_3 and H_2O, and anions, e.g. Cl′ and OH′, can take part in the co-ordination complex. In the latter case the entry of the anion causes a definite decrease in the positive valency of the complex as a whole. This may be illustrated by the well-known series of cobalt compounds derived from hexamminocobaltic chloride. The sixth member has not been prepared in the cobalt series, but is found in the parallel series of chromium compounds. The introduction of six neutral ammonia molecules leaves the valency of the cobaltic ion unchanged, but when one of these is replaced by the chloride ion the positive valency of the

$[Co(NH_3)_6]\cdots Cl'_3$ $\quad$ $[Co(NH_3)_2(NO_2)_4]'K\cdot$

$[Co(NH_3)_5Cl]\cdot\cdot Cl'_2$ $\quad$ $[Cr(H_2O)Cl_5]''K_2\cdot$

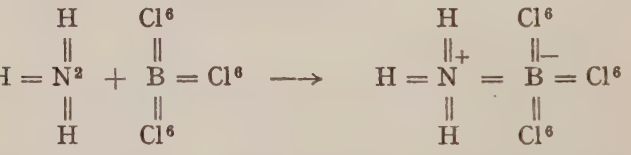
$[Co(NH_3)_4Cl_2]\cdot Cl'$ $\quad$ $[CoCl_6]'''K_3\cdot$

$[Co(NH_3)_3Cl_3]$

* *Trans. Faraday Soc.*, 1923, **19**, 469; *J.C.S.*, 1924, **125**, 132, 2672.

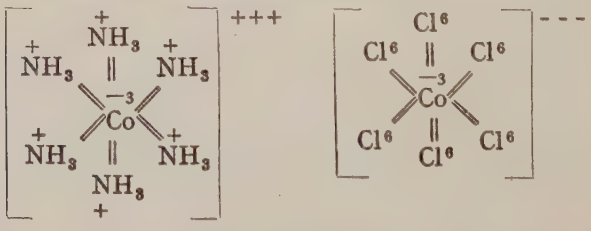
complex falls from 3 to 2. As more chlorine ions enter the complex the change in valency proceeds systematically through the unionised triamminotrichlorocobalt to potassium cobalti-chloride, in which the complex has three negative charges. This characteristic change in electrovalency is a necessary consequence of any electronic theory of the structure of these substances. The negative charge on the anion is due to an excess of electrons, and this is communicated to the complex, thus altering its net charge. In fact, the valency change merely shows that it is an anion and not a neutral group which enters the complex.

A comprehensive theory of the structure of co-ordination compounds has been developed by Sidgwick.* This is based upon the fact that all the entering groups possess at least one pair of unshared electrons which can be shared with the central atom. Thus, in the simple case of the compound $BCl_3 \cdot NH_3$, the combination can be represented thus:



Sidgwick terms the atom which supplies the pair of electrons the *donor*, and the atom which shares them the *acceptor*. Here nitrogen is the donor and boron the acceptor; the link thus formed is termed by Sidgwick a *co-ordinate* link; in this substance it is identical with a semipolar double bond.

This type of linkage is then used to account for the structure of the co-ordination complex, and gives, for the extreme members of the series of cobalt compounds described above, the following electronic formulæ I and II.



I II

* *J.C.S.*, 1923, **123**, 725.

Here the octet rule is explicitly abandoned, and shells of 12 and 16 electrons are postulated in compounds with co-ordination numbers 6 and 8.

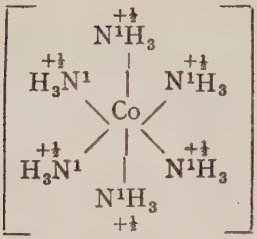
Such formulæ are obviously incompatible with the views developed in the preceding chapters of this book. The evidence in favour of the general validity of the octet rule has been discussed, and, in the author's opinion, cannot be lightly set aside. In particular, if shells with more than eight electrons are stable, it would be expected that a similar stability would be found for the shell of 18 electrons which corresponds to the filling of the M level. Using co-ordination links this would give a maximum co-ordination number of 9. No stable compounds with this co-ordination number are known, and the stable compounds with co-ordination number 8 show no tendency to acquire another group to attain this stable shell.

Another criticism of formulæ of the type of I and II is directed towards the improbable distribution of polarities within the complex ion which these structures involve. In both formulæ the cobalt atom shares 12 electrons, giving an effective charge of -6; subtracting the positive charge of three units due to the core, the net charge is -3. Similarly, the nitrogen atoms in I carry a positive charge, whilst the chlorine atoms in II are neutral. It does not seem probable that cobalt would be negative to nitrogen as in I, and still less probable that it would be negative to chlorine as in II.

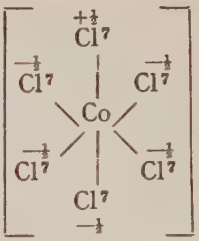
These difficulties disappear if the duplet linkages are replaced by singlets giving the formulæ III and IV. Here each cobalt atom is sharing six electrons and is neutral, whilst the positive and negative charges on the ions are evenly distributed amongst the peripheral groups. These formulæ are also capable of accounting for the stereochemical properties of these substances just as satisfactorily as I or II, for all the groups are similarly held and may occupy the corners of a regular octahedron.*

The presence of singlet linkages in co-ordination compounds should of course be capable of detection by means of the parachor, and an experimental test of the validity of formulæ

* It was originally suggested by the author (*J.C.S.*, 1927, 1180) that an octet was attained in these compounds as in formula XXVII, p. 135. Since, however, stable sextets are found in aluminium acetylacetone, etc., this view is now abandoned.



III



IV

I and II, or III and IV, can therefore be applied. The cobalt-ammines are not suitable substances for this purpose, for they cannot be fused without decomposition, but a number of other co-ordination compounds are sufficiently stable, and are discussed in the next section.

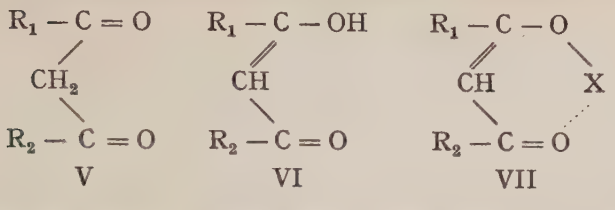
Chelated Compounds

Two or more of the groups which enter a co-ordination complex may be attached to the same molecule of an organic substance, so that a ring is formed when the groups are united to the metallic atom. Such groups are termed, by G. T. Morgan, chelate groups.*

Familiar examples are furnished by ethylene diamine, in which two NH_2 groups can unite with the central atom, and by the oxalato group in which the anion of oxalic acid gives two points of attachment to the complex. Co-ordination compounds, containing chelate groups, are usually very stable, and those derived from β-diketones and similar compounds which form six-membered rings in the complex can often be melted and even distilled without decomposition. They are, therefore, eminently suitable for the study of the parachors of co-ordination compounds.

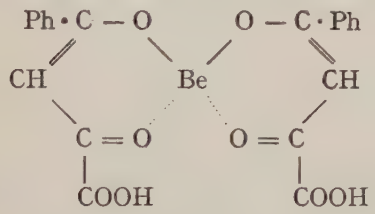
The β-diketones have the general formula V, and the formation of metallic derivatives most probably takes place by enolisation, VI, and replacement of a hydrogen atom by an equivalent of a metal X, as in VII. The metal atom is then supposed to be linked to the second oxygen atom by a

* *J.C.S.*, 1920, **117**, 1457. "The adjective 'chelate,' derived from the great claw or 'chela' of the lobster and other crustaceans, is suggested for these caliper-like groups which function as two associating units and fasten on to the central metallic atom so as to produce heterocyclic rings."



V VI VII

" residual valency " shown as a dotted line. It is clear, however, from the behaviour of these substances, that no difference in properties can be found between the normal and residual valencies. In particular, it has been abundantly proved that the residual valency is a directed valency, and can give rise to optical activity.* Thus, Mills and Gotts have resolved the beryllium, copper, and zinc derivatives of benzoyl pyruvic acid for which the structure VIII is usually written. It is evident that the four linkages to the metal,

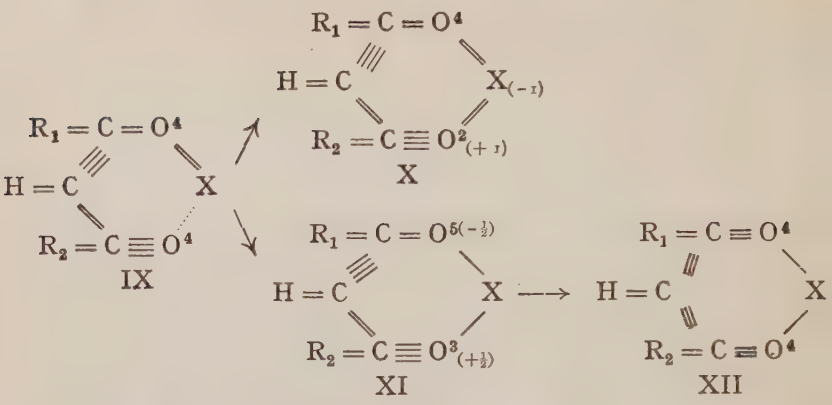


VIII

including the two residual valencies, must be arranged tetrahedrally around the metallic atom in order to produce an asymmetric molecule.

When the structure of a derivative of a β-diketone is expressed as an electronic formula, the residual valency may be written either as a singlet or a duplet linkage. Thus, starting with IX we may, following Sidgwick, write the residual valency as a co-ordinate link, in which the oxygen atom is the donor and the metal the acceptor. For metals with valencies 1, 2, 3, and 4, this gives shells of 4, 8, 12, and 16 electrons about the central atom. It involves, moreover, an unlikely distribution of polarities, for the donor, oxygen, becomes positive, and the metal negative. An alternative formula may be obtained by splitting the duplet link between the metal and oxygen in IX to give a singlet link to each oxygen atom as

* Burgess and Lowry, *J.C.S.*, 1924, **125**, 2081 ; Mills and Gotts, *ibid.*, 1926, 3121 ; Mann and Pope, *ibid.*, p. 2675.



in XI. This leaves small positive and negative charges on the oxygen atoms which can be smoothed out by rearranging the electrons in the remainder of the ring as triplet linkages as in XII; this symmetrical formula makes every atom in the molecule neutral.

The parachors of a number of such co-ordinated compounds have been determined,* and will now be considered. In the tables below, the observed parachors are used to calculate the constant for the metal, assuming (1) the singlet formula XII, and (2) the duplet formula X. In calculating Σ [P.] for the singlet formula, the constant for the six-membered ring is given its full value of 6·1. It might be supposed that the closing of a ring by singlet linkages would give a smaller increment than that found for a ring which consists entirely of duplets; from the data at present available, it does not appear that such a correction is needed.

Table 52 gives the data for thallium compounds. It will be seen that the singlet formula gives a constant for thallium (62·4) which is close to the value deduced from the unco-ordinated thallium compounds in the lower part of the table (65·5). The duplet formula gives a much lower figure (39·2), which is quite inadmissible. Further evidence in favour of the higher value given by the singlet formula is furnished by the constants for neighbouring elements in the periodic table. From mercury and its alkyl derivatives, Hg = 69, and from lead tetraethyl, Pb = 76, so that the constant for thallium should be approximately 70.

Thallous nitrate gives an abnormally high parachor which

* Sugden, *J.C.S.*, 1929, 318.

TABLE 52

Thallium Compounds

Substance.	*Formula.*	[*P.*] *obs.*	*Singlet.* Σ[*P.*]	*Tl*	*Duplet.* Σ[*P.*]	*Tl*
Thallous acetoacetic ester	$Tl(C_6H_9O_3)$	332·2	272·0	60·2	295·2	37·0
Dimethylthallium benzoylacetonate	$Me_2Tl(C_{10}H_9O_2)$	523·7	459·1	64·6	482·3	41·4
			Mean	62·4		39·2

	[*P.*] *obs.*	Σ[*P.*]	*Tl*
Thallous ethoxide	177·3	115·1	62·2
Thallous formate	150·3	80·3	70·0
Thallous acetate	183·5	119·3	64·2
Thallous nitrate	177·3	92·5	(84·8)
		Mean, excluding nitrate	65·5

is paralleled by the constants for other fused salts and metals (cf. p. 178). This figure is therefore neglected in calculating the mean. From all the remaining data the parachor for thallium appears to be 64 units.

For the beryllium compounds recorded in table 53, the singlet formula gives Be = 37·8, which lies between the values found for Li = c. 50 and B = 16·3. The duplet formula gives a negative value which cannot be accepted. It will be noted that the acetylacetonate gives a higher figure than the remaining compounds, and this requires further investigation. It is possible that this substance in the fused state contains a small proportion of molecules in which the beryllium atom is not fully co-ordinated (cf. p. 149).

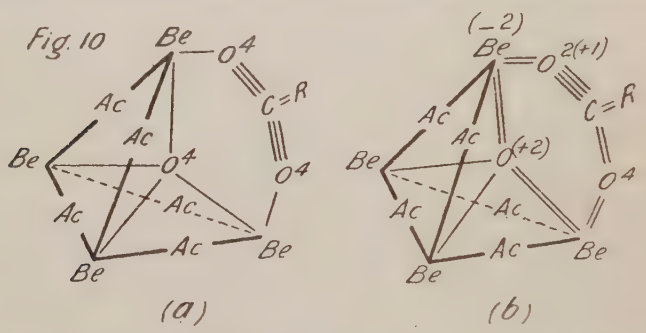
TABLE 53

Beryllium Compounds

Substance.	*Formula.*	[*P.*] *obs.*	*Singlet.* Σ[*P.*]	*Be*	*Duplet.* Σ[*P.*]	*Be*
Beryllium acetylacetonate	$Be(C_5H_7O_2)_2$	470·4	426·0	44·4	472·4	−2·0
Beryllium propionylacetonate	$Be(C_6H_9O_2)_2$	539·0	504·0	35·0	550·4	−11·4
Basic beryllium propionate	$OBe_4(C_3H_5O_2)_6$	985·4	849·6	34·0	1035·2	−12·4
			Mean	37·8		−8·6

The last compound of this element recorded in the table, basic beryllium propionate, is the second member of a peculiar series of co-ordination compounds which beryllium forms with organic acids. These substances have the general formula

$OBe_4(CO_2R)_6$, where R is an alkyl radicle. These substances have an extraordinary stability; they are readily fusible and many of them can be distilled without decomposition. These properties, coupled with their ready solubility in hydrocarbons, indicate that they are covalent compounds and not salts. The arrangement of the atoms in the molecule has been determined by a detailed X-ray study of the acetate*; it is found that the four beryllium atoms are arranged at the corners of a regular tetrahedron with the unique oxygen atom at the centre (fig. 10). The six acyl groups span the edges of the tetrahedron, and, from the high symmetry of the crystal, it is necessary to assume that the difference between the carbonyl and hydroxyl oxygen atoms is in some way smoothed out. All these facts



are readily accounted for by the singlet formula shown in fig. 10 (*a*). The structure consists of six interlocking rings of which only one is shown in detail. The two oxygen atoms are symmetrically held by triplet linkages, and all the atoms in the molecule are neutral. It is possible, of course, to write a similar formula involving duplet linkages as shown in fig. 10 (*b*); here, however, the oxygen atoms are positively charged and the beryllium atoms are negative. The parachor, given in table 53, shows conclusively that the singlet formula is correct, for it gives a reasonable value for the parachor of beryllium, whilst the duplet gives a negative value for this constant.

The aluminium compounds recorded in table 54 contain three chelate groups, and the difference between the parachors calculated for the singlet and duplet formulæ is still larger. The former gives Al = 38·6, which lies between the constants

* Sir W. H. Bragg and G. T. Morgan, *Proc. Roy. Soc.*, 1923 (A), 104, 437.

for sodium, c. 80, and silicon, c. 25. An observation by Smith* of the surface tension of the molten metal gives Al = 55; the accuracy of this measurement is probably not very high, but it indicates the order of magnitude of the constant. The negative value given by the duplet formula is quite inadmissible.

The table also includes data for aluminium bromide which presents a structural problem of some interest. The formula of this substance is undoubtedly Al_2Br_6; this is shown by its vapour density,† and its molecular weight when dissolved in

TABLE 54

Aluminium Compounds

Substance.	*Formula.*	[*P.*] *obs.*	*Singlets.* Σ[*P.*]	*Al*	*Duplets.* Σ[*P.*]	*Al*
Aluminium acetylacetonate	$Al(C_5H_7O_2)_3$	680·5	639·0	41·5	708·6	−28·1
Aluminium propionylacetonate	$Al(C_6H_9O_2)_3$	788·0	756·0	32·0	825·6	−37·6
Aluminium bromide	Al_2Br_6	457·6	373·2	42·2	419·6	+19·0
			Mean	38·6		

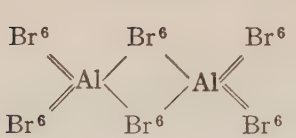
bromine‡ and in carbon disulphide.§ Solutions in nitrobenzene give lower values corresponding to $AlBr_3$, but these solutions conduct electricity, and some interaction with the solvent has evidently occurred. Fused aluminium bromide is practically a non-conductor at temperatures just above its melting point; at considerably higher temperatures a small conductivity is found, indicating that a few ions are formed. The fused substance cannot therefore be represented by the polar formula $Al^{\cdots}\ [AlBr_6]'''$, and the simplest electronic formulæ for the double molecule are shown in XIII and XIV. Here again the singlet formula XIII gives neutral molecules, whilst the duplet formula XIV makes the aluminium negative and the bromine positive. The parachor recorded in table 54 shows that the singlet formula is correct, and gives a constant

* *J. Inst. Metals*, 1914, **12**, 168.

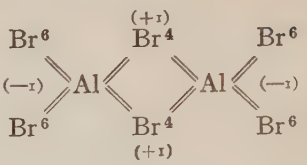
† Deville and Troost, *Compt. Rend.*, 1857, **45**, 821; *Ann. Chim. Phys.*, 1860 [3], **58**, 257.

‡ Beckmann, *Z. f. physikal. Chem.*, 1903, **46**, 853; *Z. f. anorgan. Chem.*, 1906, **51**, 96.

§ Kohler, *Amer. Chem. J.*, 1900, **24**, 385.



XIII

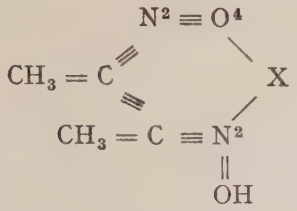


XIV

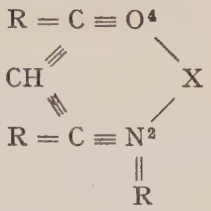
for aluminium which agrees with the value found from the co-ordinated compounds. It is interesting to note that the aluminium atom in XIII is associated with a sextet, and in XIV with an octet; hence the tendency towards neutrality in this molecule is greater than the tendency to complete an octet.

In these co-ordination compounds of monovalent, divalent, and trivalent metals, the parachor reveals the same anomaly as is found in the higher halides, and gives precisely the results which are predicted by the theory of singlet linkages. The alternative duplet formulæ cannot be retained by postulating that a correction is needed when the valency shell exceeds eight, for in the beryllium compounds such a formula gives a shell of eight electrons around the beryllium atom, and a large negative anomaly is still found in the parachor. The only way of saving the duplet formulæ appears to be the adoption of the hypothesis discussed on page 133, that the extra electrons shared each cause a contraction of 11·6 units. The grounds for rejecting this interpretation of the parachor have already been considered; it may be noted here, however, that the metallic derivatives of β-diketones provide a further argument against the duplet formulæ from the improbable intramolecular polarities which they involve. Thus the duplet formula for aluminium acetylacetonate postulates an aluminium atom with three *negative* charges attached to three *positive* oxygen atoms; the singlet formula makes all the atoms in the molecule neutral.

The singlet structures assigned to the acetylacetonates, etc., can obviously be used to account for the metallic derivatives of dioximes, iminoketones, etc., as in formulæ XV and XVI. It is noteworthy that the majority of stable compounds of this type contain six-membered rings; the residual charges on the atoms co-ordinated to the metal can therefore be smoothed out by the redistribution of electrons to give four triplet links instead of alternate duplets and quartets



XV



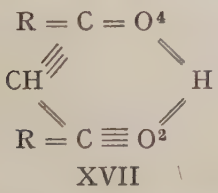
XVI

(cf. p. 144). The attainment of completely neutral molecules in this manner may be connected with the remarkably high stability of these co-ordination compounds.

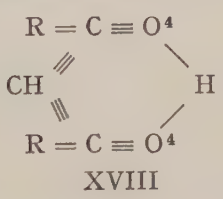
Unco-ordinated Derivatives of β-Diketones

In a number of cases it has been found that the parachors of certain derivatives of β-diketones do not show the decrement expected for the singlet linkages, and indicate that the substance examined has a normal open chain structure for the diketone residue. Some examples of this behaviour are collected in table 55 and include the free diketones as well as certain metallic derivatives.

It has been supposed by many workers that hydrogen could acquire a shell of four shared electrons, and thus close the ring in the same manner as a metallic atom (formula XVII). This formula or any other formula in which more than two electrons are associated with the hydrogen atom is open to grave



XVII



XVIII

objections from the standpoint of modern theories of atomic structure. The K level cannot contain more than two electrons, for if more are added, two or more electrons in the atom will have the same four quantum numbers in contradiction of Pauli's principle (p. 70). This objection does not apply to the singlet formula XVIII ; it is therefore possible for the free diketones to form a co-ordinated ring by means of a hydrogen atom.

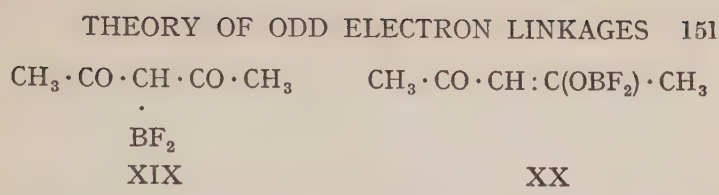
TABLE 55

Unco-ordinated Derivatives of β-Diketones

Substance.	*Formula.*	[*P.*]*obs.*	[*P.*] *calc.* *Co-ordinated.*	*Open chain.*
Acetylacetone	$C_5H_8O_2$	245·4	230·1	247·2
Propionylacetone	$C_6H_{10}O_2$	279·7	269·1	286·2
Benzoylacetone	$C_{10}H_{10}O_2$	382·4	364·0	381·1
Acetylacetone boron difluoride	$(C_5H_7O_2)BF_2$	300·6	280·4	297·5
bis-Acetylacetone tin dichloride	$(C_5H_7O_2)_2SnCl_2$	617·2	592·5	626·7

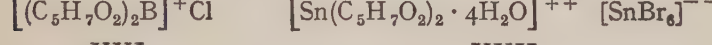
The parachors of the diketones so far examined indicate that little or no co-ordination by means of hydrogen takes place. Some of the substances referred to in table 55 show a small deficiency in the parachor, which may be due to an equilibrium mixture of the co-ordinated and open chain forms. Since the parachors are determined in the liquid state, a dynamic isomerism of this type is possible. The problem is complicated, however, by the presence of the enolic isomeride, which, since it possesses a free hydroxyl group, would behave as an associated liquid and give a parachor a few units lower than the calculated figure. Unless the substance is entirely in the enol form this effect would be small, so that the decrements observed for substances, e.g. propionylacetone, probably indicate the presence of a small proportion of the co-ordinated isomeride. When a wider range of substances has been studied the parachors should give some interesting information as to the conditions which favour co-ordination. From the results at present available it will be seen that acetylacetone and benzoylacetone show no evidence of co-ordination, whilst propionylacetone is appreciably co-ordinated. It is noteworthy that the metallic derivatives of the first two substances give abnormally high constants for the metals when complete co-ordination is assumed (cf. tables 52 and 54) ; these high values may be due to the presence of a small amount of the open chain isomeride in the fused substance.

The results found for the boron and tin compounds are quite unexpected, but show clearly that these substances consist essentially of the open chain isomeride. The boron atom may be attached to either carbon, XIX, or oxygen, XX ;



XIX XX

since acetylacetone is easily regenerated from these substances by hydrolysis, XX is the more probable formula. It is evident from these results that a metallic derivative of a β-diketone is not necessarily a cyclic co-ordination compound, and an interesting field for further investigation is suggested by a study of the conditions which favour or inhibit cyclic co-ordination in metallic derivatives of this type. The nature of the halogen atom attached to the metal appears to play an important part. Thus, in the boron series, the fluoride gives the unco-ordinated derivative with one acetylacetone residue, whilst the chloride gives *bis*-acetylacetone boronium chloride, XXI, which, since it is a salt giving chlorine ions, is probably



XXI XXII

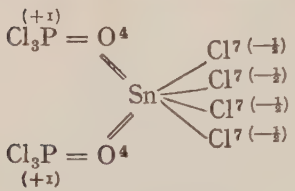
co-ordinated. Similarly in the tin series, the chloride gives the unco-ordinated compound, and the bromide in the presence of moisture gives the complex salt XXII.* The structure of the latter substance has not yet been elucidated; if the acetylacetone residues are co-ordinated to the tin atom, the latter will have a co-ordination number of eight.

Molecular Compounds

It is convenient to include here an account of investigations on certain additive compounds which are not readily formulated on the older theories of valency, and are often termed molecular compounds. The first of these is a compound of stannic chloride and phosphorus oxychloride, discovered by Casselmann,† who gave it the formula $SnCl_4 \cdot POCl_3$, and described the substance as a white crystalline solid, melting at 54° and boiling at 180°. A re-examination of this substance shows that it has the composition $SnCl_4 \cdot 2POCl_3$, melts at 54°, and boils at 118°.‡ The possible electronic structures for this substance are shown below, together with the predicted

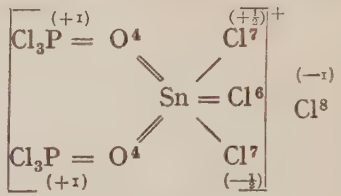
* Morgan and Drew, *J.C.S.*, 1924, **125**, 375.
† *Ann.*, 1852, **83**, 257; 1856, **98**, 213.
‡ Garner and Sugden, *J.C.S.*, 1929.

parachors. In XXIII the four chlorine atoms in stannic chloride are supposed to become linked by singlets, thus



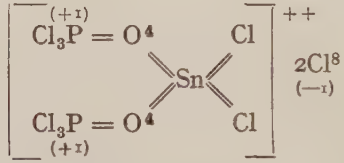
[P.] calc. 665·4

XXIII



[P.] calc. 688·6

XXIV



[P.] calc. 711·8

XXV

leaving room for the sharing of a lone pair from the oxygen atom of the phosphorus oxychloride. The singlet linkage can always be replaced by a polar bond, and, by the successive ionisation of two chlorine atoms, formulæ XXIV and XXV are obtained. The parachors calculated for these formulæ are markedly different, and the value found by experiment for this substance, 689·7, indicated that its structure should be represented by formula XXIV. This result was somewhat surprising, since the additive compound is readily volatile and soluble in hydrocarbon solvents, and would not therefore be regarded as a salt. The electrical conductivity of the fused substance was therefore determined, and it was found to be very small; at 60° the specific conductivity is less than 8×10^{-5} mhos. The ionised formula XXIV is therefore excluded. The observed parachor is, however, larger than that predicted for the covalent formula XXIII. This can be explained by assuming that the *solid* substance has this structure and that fusion causes partial dissociation into $SnCl_4$ and $POCl_3$. This interpretation is supported by the fact that some decomposition takes place on distillation; the first fractions of the distillate do not solidify completely and contain an excess of the more volatile component $SnCl_4$.

Another series of additive compounds, which have been found to possess a somewhat similar structure, is furnished by the double mercuric sulphonium iodides of the general formula $R_2S{\cdot}RI{\cdot}HgI_2$. Of these the compounds derived from benzyl sulphide, described by Smiles,* were found to be fusible without decomposition, and have been examined in detail.† These substances are typical salts and give highly conducting solutions in acetone and acetonitrile. The molecular weights of the methyl and ethyl dibenzyl mercuric sulphonium iodides, determined in acetone by the ebullioscopic method, are given in table 56, and show that two ions are present. This conclusion is confirmed by the conductivities of acetone solutions of these salts recorded in table 57, which agree closely with those of other binary salts with complex cations,

TABLE 56

Molecular Weights of Double Mercuric Sulphonium Iodides in Acetone

$(C_7H_7)_2S{\cdot}CH_3I{\cdot}HgI_2$ $M = 810$			$(C_7H_7)_2S{\cdot}C_2H_5I{\cdot}HgI_2$ $M = 824$		
Concⁿ. gm./L.	*M. obs.*	*M. obs./M.*	*Concⁿ. gm./L.*	*M. obs.*	*M. obs./M.*
114·0	572	0·71	88·2	584	0·71
66·1	569	0·70	50·4	590	0·72
32·1	541	0·67	38·5	549	0·67

e.g. tetrapropyl ammonium iodide and picrate, measured in acetone solution by Walden, Ulich, and Birr.‡ It is evident that the double sulphonium iodides must also be regarded as binary electrolytes.

TABLE 57

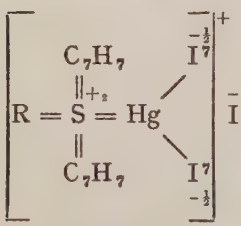
Conductivities of Double Mercuric Sulphonium Iodides in Acetone

$(C_7H_7)_2S{\cdot}CH_3I{\cdot}HgI_2$		$(C_7H_7)_2S{\cdot}C_2H_5I{\cdot}HgI_2$		$N(C_3H_7)_4I$		$N(C_3H_7)_4{\cdot}C_6H_2(NO_2)_3O$	
Dilution	$\lambda 28{\cdot}5°$	*Dilution*	$\lambda 28{\cdot}5°$	*Dilution*	$\lambda 25°$	*Dilution*	$\lambda 25°$
100L.	114	100L.	118	100L.	112·6	500L.	125·9
500	137	400	136			1000	133·9
1250	148	1200	145				
3200	153	3000	152				

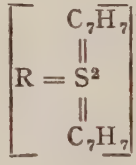
* *J.C.S.*, 1907, **91**, 1398.
† Cavell and Sugden (unpublished work).
‡ *Z. f. physikal. Chem.* 1927, **131**, 34.

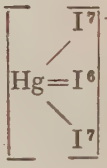
When the conductivities of the double iodides are plotted against the square root of the concentration, the plot is linear ; furthermore, the slope of the curve agrees closely with that predicted by the theory of Onsager,* thus indicating that these salts are completely dissociated.

These double mercuric sulphonium iodides can be prepared by direct combination between sulphonium iodides and mercuric iodide ; it is therefore highly probable that all three alkyl groups are attached to the sulphur atom. Furthermore, it was noted by Pope and Neville† that optically active sulphonium salts can be converted into the bromide, chloroplatinate, etc., without losing their activity, but racemise completely when the double mercuric iodide is formed. This behaviour indicates that the asymmetric sulphur atom takes part in the formation of the complex ion. The simplest formula which gives two ions, and accounts for the chemical



XXVI





XXVII

and stereochemical properties of these substances, is XXVI, which contains two singlet linkages and a duplet link between the mercury and sulphur atoms. This structure is in good agreement with the parachors found for the ethyl, n-propyl, and n-butyl derivatives given in table 58 ; if the decrement for the two singlet linkages is not included, [P.] calc. is much larger than [P.] obs.

The conductivities, molecular weights, and parachors are all compatible with formula XXVII as well as XXVI. If, however, it is assumed that the anion is HgI_3, no explanation of the racemisation of the active sulphonium compounds on formation of the mercuri-iodides is possible. The corresponding selenium compounds are also racemised when they combine with mercuric iodide, but certain optically active quaternary

* *Physikal. Z.*, 1926, **27**, 288 ; 1927, **28**, 277.
† *J.C.S.*, 1902, **81**, 1557.

TABLE 58

Parachors of Double Mercuric Sulphinium Iodides

Substance.	*Formula.*	[*P.*] *obs.*	[*P.*] *calc.*
Ethyl dibenzylsulphinium mercuri-iodide	C_2H_5 $\diagdown$ $\Vert$ SHgI$_3$ $\diagup$ $(C_7H_7)_2$	915·2	918·5
n-Propyldibenzylsulphinium mercuri-iodide	C_3H_7 $\diagdown$ $\Vert$ SHgI$_3$ $\diagup$ $(C_7H_7)_2$	952·0	957·5
n-Butyldibenzylsulphinium mercuri-iodide	C_4H_9 $\diagdown$ $\Vert$ SHgI$_3$ $\diagup$ $(C_7H_7)_2$	999·9	996·5

ammonium salts give active double mercuric iodides.* In these compounds the HgI_3 ion is probably formed.

General Conclusions

From the investigations described in this and the preceding chapter it seems probable that singlet linkages play an important part in the structure of co-ordination compounds and the so-called molecular compounds. At present only a few substances have been studied in detail, and much further work will have to be done before any general principles governing the structure of these complex compounds can be established. Nevertheless, it seems worth while to use the data at present available to draw some tentative conclusions; these will at least be of value in suggesting the direction in which further research can most fruitfully be carried out.

In the first place, it appears that stable outer shells of four and six, as well as eight electrons, must be accepted when these give rise to a neutral atom. Such shells are consequently to be expected with the elements of the first three groups of the periodic table, and for the lower valencies of transition elements. Such shells have long been recognised in simple compounds, e.g. BCl_3, but are not common because the simpler compounds of these elements are usually ionised; they are,

* Pope and Neville, loc. cit.

however, an essential feature in the structure of the co-ordination compounds as is shown by the formulæ for the acetylacetonates. The double sulphonium iodides furnish another example ; in formula XXVI the mercury atom is surrounded by a shell of four electrons, although an octet could readily be attained by linking all three iodine atoms to mercury by duplet linkages. This would give the mercury atom a net charge of -2, and the parachors and conductivities show clearly that this does not happen. Here the tendency towards the neutralisation of intramolecular charges is stronger than the tendency towards octet formation.

In the substances so far examined singlets have been found between the following pairs of atoms.

P — Cl	Al — O
Sb — Cl	Al — Br
Tl — O	Sn — Cl
Be — O	Hg — I

One of the elements taking part in the link is a halogen or oxygen, and the other element is usually a metal. This suggests that a singlet link is more stable when it joins two elements which differ markedly in their electron affinity. Connected with this behaviour is the conception of a singlet linkage as a half-way stage between a covalency and an electrovalency, e.g.

$$\underset{\text{XXVIII}}{X = Cl^{6}} \longrightarrow \underset{\text{XXIX}}{\overset{(+\frac{1}{2})}{X} - \overset{(-\frac{1}{2})}{Cl^{7}}} \longrightarrow \underset{\text{XXX}}{\overset{(+1)}{X}\ \overset{(-1)}{Cl^{8}}}$$

Thus the ionisation of a salt in solution may be due to a change from XXVIII through XXIX to XXX, in which the co-ordination of solvent molecules with the cation $X^{\cdot}$ may be one of the conditions which favour ionisation.

CHAPTER VIII

ASSOCIATED LIQUIDS

Normal and Associated Liquids

LIQUIDS can be classified broadly into two groups, which are usually distinguished by the terms "normal" and "associated" liquids. The latter show a number of abnormalities in their physical properties, which are usually explained by the formation of aggregates of simple molecules to give an easily dissociated complex. Association is thus distinguished from polymerisation, in which definite chemical combination takes place and is not easily reversed. Acetylene, for example, polymerises to benzene, but the latter is not regarded as an associated form of acetylene, for the reverse change does not readily occur. It is noteworthy that, with the exception of the lower organic acids, associated liquids give very little indication of association in the state of vapour.

The chief physical properties which are used to diagnose association in the liquid state are :—

(a) Abnormal surface tension relationships.
(b) Abnormal critical ratios.
(c) High latent heats of evaporation.
(d) High dielectric constants.
(e) Abnormal molecular weights in solution.

These will be considered briefly in this order.

Ramsay and Shields* found that a number of normal liquids gave a constant rate of decrease of molecular surface energy with temperature, i.e.

$$\frac{d}{dT}\left[\gamma\left(\frac{M}{D}\right)^{2/3}\right] = k = 2{\cdot}12 \ldots\ldots\ldots\ldots\ldots (1)$$

Here γ is the surface tension, M the molecular weight, and D the density. In table 59 the first four liquids are normal and the second four associated. The latter give lower values of k, which can be accounted for by supposing that x molecules

* *J.C.S.*, 1893, **63**, 1087.

have associated to form a complex, so that M in equation (1) should be replaced by xM. Hence the degree of association, x, can be calculated from the observed value of k by the formula

$$x = \left(\frac{2{\cdot}12}{k}\right)^{3/2} \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

The values of x thus obtained are given in table 59; for the first group x is very nearly unity, and these substances are regarded as normal liquids. The second group gives values of x which indicate that three or more molecules have united to form a complex molecule.

Later work has shown that the value of k for normal liquids is not constant, but depends upon the size and constitution of the molecule. In particular, larger molecules give values of k greater than the standard figure 2·12; some examples are given in the last four lines of table 59, and the application of equation (2) indicates that these substances are *dissociated* in the liquid state. It is, of course, highly improbable that these stable substances are dissociated, and it must be concluded that k is not a general constant, but varies from substance to substance. The chief factor which seems to determine k for organic substances is the size of the molecule, and for normal substances containing less than 12 carbon atoms in the molecule, k is usually between 2·0 and 2·5. For molecules of this size a low value of k may perhaps be taken as

TABLE 59

Ramsay-Shields Constants

Substance.	k	x
Benzene	2·10	1·01
Nitrobenzene	2·23	0·93
Ether	2·01	1·08
Carbon tetrachloride	2·21	0·94
Water	1·04	2·91
Methyl alcohol	0·93	3·44
Ethyl alcohol	1·08	2·75
Acetic acid	0·98	3·18
Benzophenone	2·90	0·63
Tribenzylamine	3·50	0·47
Amyl stearate	3·82	0·41
Tristearin	5·95	0·21

a qualitative indication of association, but its quantitative significance is very doubtful.

Observations on fused metals and salts give still more remarkable values for the Ramsay-Shields constant ; some examples are given in table 60. The small values might be interpreted as due to a high degree of association, but negative values of this constant are actually found in this group of substances, i.e. the molecular surface energy increases with rising temperature. It is evident that the Ramsay-Shields constant is

TABLE 60

Ramsay-Shields Constants for Fused Metals and Salts

Substance.	*k*	*Substance.*	*k*
Mercury [1]	0·96	NaF [3]	0·52
Tin [2]	—0·10	Na_2SO_4 [3]	0·30
Lead [2]	0·22	$NaNO_3$ [3]	0·24—0·61
Bismuth [2]	0·27	KCl [3]	0·68
Cadmium [2]	—2·10	KPO_3 [3]	0·91
,,	0·20	K_2SO_4 [3]	0·90
Antimony	0·02	AgCl [4]	0·66

(1) Harkins and Ewing, *J. Amer. Chem. Soc.*, 1920, **42**, 2539.
(2) Bircumshaw, *Phil. Mag.*, 1927 [7], **3**, 1286.
(3) Jaeger, *Z. f. anorgan. Chem.*, 1917, **101**, 1.
(4) Lorentz, Liebmann, and Hochberg, *ibid.*, 1916, **94**, 301.

profoundly affected by other factors than association ; consequently a low value of k may not indicate association, but may be due to the action of the unknown factors which are operative to such a marked degree in fused metals and salts.

Another method of using surface tension data to detect association has been devised by Walden,* who found that for normal liquids

$$\frac{Ma^2}{T} = K = 1{\cdot}162$$

Here M is the molecular weight, and a^2 the specific cohesion $\left(=\frac{2\gamma}{gD}\right)$ at the boiling point T. Associated liquids give low values of K, and the degree of association is calculated by the ratio $1{\cdot}162/K$. Table 61 gives some examples of the use of this function.

* *Z. f. physikal. Chem.*, 1908, **65**, 129, 257 ; *Z. f. Elektrochem.*, 1908, **14**, 713.

TABLE 61

Molecular Cohesion at the Boiling Point (Walden)

Normal Liquids.			*Associated Liquids.*		
Substance.	$Ma^2/T.$	x	*Substance.*	$Ma^2/T.$	x
Stannic chloride	1·18	0·98	Water	0·586	1·98
Chloroform	1·12	1·04	Methyl alcohol	0·483	2·4
Benzene	1·15	1·01	Ethyl alcohol	0·685	1·8
Nitrobenzene	1·13	1·02	Formic acid	0·651	1·78
Pyridine	1·13	1·02	Acetic acid	0·594	1·95

Walden gives a similar formula for the molecular cohesion at the freezing point, which for normal substances gives $K = 3{\cdot}65$. This method of determining the degree of association leads to some very curious results; thus benzene and naphthalene are found to be highly associated at their freezing points. Since melting points are markedly affected by small changes in constitution, they cannot be accepted as even a rough approximation to corresponding temperatures, so that it is not surprising that Walden's freezing point formula leads to erroneous results.

The second method of detecting association involves a knowledge of the critical constants so that it is applicable only to substances which do not decompose at the critical temperature. According to van der Waals' equation, the ratio RT_c/P_cV_c should be constant for all substances, and should have the value 2·67; according to Dieterici's equation of state, this ratio should be 3·695. From the values of this critical ratio, quoted in table 62, it will be seen that most normal liquids give a value of about 3·7, but that hydrogen and helium give abnormally small ratios. On the other hand, associated liquids give critical ratios which are larger than the

TABLE 62

Critical Ratios and Association

Normal Liquids.		*Associated Liquids.*	
Substance.	RT_c/P_cV_c	*Substance.*	RT_c/P_cV_c
Helium	3·04	Water	4·35
Hydrogen	3·21	Methyl alcohol	4·61
Oxygen	3·44	Ethyl alcohol	4·25
n-Pentane	3·77	Acetic acid	5·01
Benzene	3·75		
Chlorobenzene	3·75		

normal value. Since the critical ratio for normal substances varies over a considerable range, it is difficult to use this ratio in order to deduce the degree of association. E. E. Walker* has attempted a solution of this problem by correlating the change in the value of the critical ratio for normal substances, with changes in the length of the molecule; the latter is supposed to be an additive function of the atoms concerned. By comparing the observed critical ratios with those calculated from the length of the molecule, the degree of association is obtained. The results of this method of calculation are in general very similar to those found by Walden; alcohols and acids are found to be highly associated, but the degree of association is rather less than that given by the Ramsay-Shields method.

An important relation between the latent heat of evaporation and the temperature at which a liquid boils was discovered by Trouton,† and is usually known as Trouton's rule. It is given by the simple formula

$$Ml/T = constant$$

where M is the molecular weight, l the latent heat of evaporation per gram, and T the boiling point on the absolute scale. For many liquids Trouton's ratio is nearly 21 (cf. table 63).

TABLE 63

Trouton's Rule

Normal Liquids. *Substance.*	Ml/T	*Associated Liquids.* *Substance.*	Ml/T
Hydrogen	12·2	Acetic acid	13·8
Oxygen	18·6	,, ,,	(27·6)
Ether	21·1	Ethyl alcohol	26·9
Benzene	21·2	Water	25·9
Propyl acetate	22·2		

Hydrogen gives an abnormally low constant and, for normal liquids, the Trouton constant tends to increase when more complex substances with higher boiling points are studied. Associated liquids tend to give higher values, and this may be explained as the result of the energy which is needed to break up the complex molecules in the liquid to give the simple molecules found in the vapour. Acetic acid is an exception, and has a low Trouton constant. Since the vapour near the

* *Phil. Mag.*, 1924 [6], **47**, 111. † *Ibid.*, 1884 [5], **18**, 54.

boiling point consists chiefly of double molecules, some writers take M for this substance as 120 $\left[(C_2H_4O_2)_2\right]$; this makes the Trouton constant 27·6 and brings acetic acid into line with the other associated substances.

A more accurate form of Trouton's rule has been developed by Hildebrand,* who considers that the boiling point is not a suitable temperature at which to compare latent heats. Although the pressure of the vapour is constant for all liquids at the boiling point, the concentration of the vapour is not constant, but depends upon the absolute temperature at which the liquids boil. Thus the saturated vapour of a liquid with a high boiling point will contain fewer molecules in unit volume than the vapour of a liquid which boils at a lower temperature. Hildebrand makes a correction for this effect by calculating, from the vapour pressure-temperature curves, the latent heat at temperatures which give vapours having a constant concentration of molecules. He then finds that Ml/T is really constant over a wide temperature range. Some examples are given in table 64, which gives the values of this ratio when the vapour has a concentration of 0·005 gm. mols./L. Here again the associated liquids are found to give high values.

TABLE 64

Hildebrand's Relation

Normal Liquids.			*Associated Liquids.*		
Substance.	*T.*	*Ml/T.*	*Substance.*	*T.*	*Ml/T.*
Nitrogen	55°A.	27·6	Ammonia	200°A.	32·4
Chlorine	194°	27·8	Water	325°	32·0
Hexane	294°	27·0	Ethyl alcohol	307°	33·4
Stannic chloride	329°	27·2			
Mercury	560°	26·2			
Cadmium	988°	26·4			
Zinc	1130°	26·4			

Water, alcohols, and the lower fatty acids all possess a high dielectric constant, and this is sometimes regarded as a test for association. However, many normal liquids, e.g. nitrobenzene, also give high values for this constant. The analysis of dielectric constants in terms of electric moments, discussed in chapter V (p. 102), shows that the dielectric constant of a liquid is not a true measure of the dipole moment

* *J. Amer. Chem. Soc.*, 1915, **37**, 970.

of its molecules, but is usually much smaller because of dipole association. Further, the electric moment of the molecule, when such effects are eliminated, does not show any simple connexion with the occurrence of association in the liquid state. Thus, for a few typical normal and associated liquids, the following dipole moments are found.

Normal Liquids. *Substance.*	$\mu \times 10^{18}$	*Associated Liquids.* *Substance.*	$\mu \times 10^{18}$
Benzene	0·06	Water	1·98
Acetone	2·70	Methyl alcohol	1·78
Nitrobenzene	3·75	Ethyl alcohol	1·85

It is evident that this property is not of much use for the diagnosis of association in the liquid state.

Further evidence that particular types of molecules tend to associate can be obtained from a study of molecular weights in solution. In considering the data obtained in this way two facts must be borne in mind. In the first place, dilution, even with an inert solvent, would be expected to diminish the degree of association, so that a small amount of association found in solution may correspond to a high degree of association in the pure liquid. Next, the affinity between the solute and solvent has often an important perturbing effect. Thus the alcohols, dissolved in benzene, give molecular weights of several times the normal value, whilst with water as solvent their molecular weights are normal. Many salts show a peculiar behaviour, since in water they are dissociated into ions, whilst in other solvents, e.g. chloroform, they are highly associated. In general, it is found that if the solvent is itself a normal liquid the dissolved substance may give abnormally high molecular weights if it has itself any tendency to associate ; if, however, the solvent is an associated liquid, the molecular weight found for the solute is usually normal, or even less than normal, when ionisation takes place.

High molecular weights found in solution cannot always be accepted without question. In the freezing point method, if solid solutions are formed between solvent and solute, the observed depression will be too small, and in certain cases a rise in freezing point is found, e.g. β-naphthol dissolved in naphthalene. The occurrence of solid solutions will therefore give high values for the molecular weight. Fortunately such cases are rare, as solid solutions are usually confined to pairs

of substances which have a very similar constitution. Another source of error is the formation of colloidal aggregates in solution such as are found in the soap solutions studied by McBain and his co-workers. To illustrate this point we may consider the freezing point depressions found for potassium oleate solutions,* from which the molecular weight of the solute and its degree of association are calculated in the usual manner in table 65. From these data alone it would appear that triple molecules were present in the more concentrated solutions.

TABLE 65

Molecular Weight of Potassium Oleate ($M = 320$) in Aqueous Solution

*Conc*ⁿ.	0·1*N*	0·2*N*	0·4*N*	0·5*N*	0·6*N*
$\Delta t/1{\cdot}858$	0·045	0·064	0·116	0·15	0·19
M. calc.	698	1000	1104	1070	1010
x	2·18	3·13	3·45	3·34	3·16

An exhaustive study of these solutions shows, however, that they have a complex constitution and contain potassium ions, and colloidal aggregates of the fatty acid anion as well as colloidal particles of neutral soap. These colloidal constituents, consisting of aggregates of ten or more simple molecules or ions, may be said to owe their existence to the small affinity between the solvent, water, and the anion, which is largely a hydrocarbon chain, and also to the large affinity between such hydrocarbon chains which is also shown by the properties of thin films on a water surface. The solubility of soaps in water may be ascribed to the great affinity of the cation, sodium, or potassium, for water, and this is great enough to drag the " insoluble " anion into solution, where it then forms colloidal aggregates. It seems probable that the abnormal molecular weights found for other salts, e.g. alkyl ammonium halides in chloroform (p. 176), may be accounted for in a similar manner by the formation of colloidal aggregates. Here, again, it is the cation which has a large affinity for the solvent.

A number of other empirical relations between the properties of liquids have been used to detect association in the liquid state, but need not be considered here. For fuller information Turner's monograph on the subject should be consulted.†

* McBain, Laing, and Titley, *J.C.S.*, 1919, **115**, 1290.

† *Molecular Association*, W. E. S. Turner, Longmans, Green and Co., London, 1915.

From a general survey of the results given by these methods of detecting association in the liquid state, it is evident that certain types of liquids, notably the lower alcohols and fatty acids, respond to every test for association and can be contrasted with the hydrocarbons and their halogen derivatives which in every respect behave as normal liquids. The degree of association of a particular substance is more difficult to determine ; the methods of measuring this quantity give very variable results, and it must be concluded that at present we have no accurate method of determining molecular weights in the liquid state. A few rough conclusions can, however, be drawn as to the effect of constitution. Thus a free hydroxyl group invariably gives rise to the anomalies in physical properties which are interpreted as association, but the effect diminishes rapidly as a homologous series is ascended. The NH group in ammonia and the simpler amines appears to give a similar but rather smaller effect. The condition of the lower aldehydes, ketones, nitriles, and esters is more debatable ; in many respects these substances behave as normal liquids, but the surface tension methods indicate a small degree of association.

Remarkable discrepancies are found for fused metals. Thus mercury gives a low Ramsay-Shields constant ($k = 0{\cdot}65$) but a normal value in Hildebrand's latent heat function (p. 162), and is monatomic as vapour, and when dissolved in other metals. Similarly, lead, cadmium, and tin, which give highly abnormal Ramsay-Shields constants, give monatomic vapours and normal molecular weights when dissolved in mercury.* It is noteworthy that fused metals (and fused salts, in which similar anomalies are found) have very high surface tensions of 200–1000 dynes/cm. ; the simpler empirical relations found for liquids of lower surface tension would be expected to need some modification for the high values of the internal pressure indicated by these high surface tensions.

The Parachor and Association

The substances whose parachors have been discussed in the preceding chapters are for the most part normal liquids. For associated liquids it is usually found that the parachor is not independent of the temperature of measurement, but increases

* Ramsay, *Z. f. physikal. Chem.*, 1889, **3**, 360 ; Meyer, *ibid.*, 1891, **7**, 484.

as the temperature rises. It is convenient to group associated liquids into two classes of non-conductors and conductors. The first class includes the alcohols and acids which give parachors a few units lower than the calculated figures, whilst the parachors of the second group, which includes fused metals and salts, show large positive and negative anomalies.

In the non-conducting group it would be expected that the deviations from the predicted parachor could be accounted for by the structure of the complex molecules which are usually supposed to be present in these liquids. If the linkages which hold the associated molecules together are chemical single bonds, then the parachor would not show any change. If multiple bonds are concerned in the complex, then association should produce an increase in the parachor; if association involves the appearance of singlet linkages, then the parachor will be lower than the calculated value.

A good example of the first case is provided by the element sulphur, for which careful measurements of the surface tension and density from the melting point to the boiling point have been made by Kellas.* This element has undoubtedly a great tendency to polymerise; its vapour near the boiling point consists chiefly of S_8 molecules, and its molecular weight in a number of solvents indicates a complexity varying from S_6 to S_8. The Ramsay-Shields constant from 116°–160° also gives S_6; at 160° the change to the dark viscous form occurs, and between this temperature and the boiling point the Ramsay-Shields constant indicates a complexity of S_{18}. The Walden constant at the boiling point ($Ma^2/T.$) gives, however, a complexity of $S_{5\cdot2}$. The parachors, calculated per sulphur atom by taking $M = 32$, are given in table 66.

It will be seen that in spite of the high degree of polymerisation, and the marked changes which take place in the properties

TABLE 66

Parachor of Liquid Sulphur

Temp.	γ	$D.$	*Parachor.*	
116·4	59·48	1·807	49·2	Mobile S_λ
132·0	57·72	1·795	49·1	
142·8	56·77	1·787	49·2	
155·6	55·08	1·776	49·1	

* *J.C.S.*, 1918, **113**, 903.

Parachor of Liquid Sulphur—contd.

Temp.	γ	*D.*	*Parachor.*	
183·5	54·69	1·765	49·3	Viscous S_μ
211·0	52·83	1·751	49·3	
241·0	50·51	1·734	49·2	
280·0	48·56	1·710	49·4	
302·0	47·31	1·699	49·4	
357·0	44·27	1·657	49·8	
445·0	39·87	1·605	50·1	

[*P.*] *calc.* = 49·2

of the liquid, the parachor remains constant and has very nearly the value found for sulphur in organic compounds. This behaviour is readily explained by assuming that the bonds between the sulphur atoms are all duplet linkages. If, for example, it is supposed that six-membered rings are formed as in formula I, then the parachor per sulphur atom calculated for this structure is $(6 \times 48{\cdot}2 + 6{\cdot}1) \div 6 = 49{\cdot}2$, which is very close to the observed figure. It must be remembered that the possible error in the parachors is at least $\pm$ 1 unit, and a number of similar formulæ containing larger and smaller rings could be written which would give a similar agreement; the six-membered ring seems, however, to be the most probable.

I

In the non-conducting class of associated liquids, positive anomalies have so far not been found, but the typical members of this group, the alcohols and acids, show a negative anomaly. For three substances data are available over a wide range of temperatures (table 67), and show a steady increase of parachor as the temperature rises.

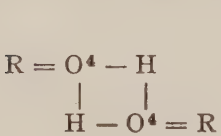
TABLE 67

*Parachors of Lower Alcohols and Acids.**

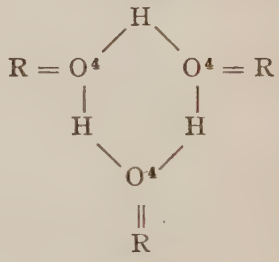
Methyl Alcohol.					*Ethyl Alcohol.*				*Acetic Acid.*			
		[*P.*]				[*P.*]				[*P.*]	
t.	*Obs.*	*obs.*	*Anomaly.*	*t.*	*Obs.*	*obs.*	*Anomaly.*	*t.*	*Obs.*	*obs.*	*Anomaly*
65	S.	86·7	−6·5	−57	S.	124·2	−8·0	10	S.	131·3	−9·9
35	S.	86·8	−6·4	−30	S.	125·4	−6·8	50	S.	131·7	−9·5
0	S.	87·9	−5·3	0	S.	126·4	−5·8	100	S.	132·2	−9·0
20	R. & C.	88·3	−4·9	20	R. & C.	126·9	−5·3	130	R. & S.	132·8	−8·4
70	R. & S.	89·3	−3·9	80	R. & S.	128·8	−3·4	190	,,	134·0	−7·2
30	,,	90·6	−2·6	140	,,	129·7	−2·5	250	,,	135·6	−5·6
90	,,	91·9	−1·3	200	,,	131·0	−1·2	280	,,	137·0	−4·2
[*P.*] *calc.* = 93·2					[*P.*] *calc.* = 132·2				[*P.*] *calc.* = 141·2			

* For data and observers, see Sugden, *J.C.S.*, 1924, **125**, 37.

The negative anomalies found suggest at once that singlet linkages are present in the complex molecules, whilst the decrease in the anomaly with rising temperature suggests that association is by no means complete, but diminishes rapidly at higher temperatures. When an attempt is made to write formulæ for the complex molecules, it is found that a large number of alternative structures are possible, and since we have no accurate knowledge of the degree of association, it is not easy to distinguish between them. The simplest and most obvious hypothesis is that of co-ordination by means of the hydrogen atoms, as in formulæ II and III, which give parachor anomalies of — 17·4 and — 21·2 (per single molecule) respectively for complete association. Assuming, for instance,



II



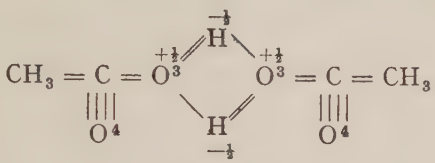
III

that the complex molecule in the alcohols is represented by III, then the alcohols at room temperature contain about 30% of triple molecules, which would correspond to an average molecular weight 1·25 times the normal value. This is much smaller than the degree of association given by the Ramsay-Shields or Walden constants, but we have already seen that these methods cannot be regarded as giving more than a qualitative indication of association. It should be noted that in the free β-diketones (p. 150), where a hydrogen atom may be co-ordinated with two oxygen atoms in the same molecule by means of singlet linkages, the parachor shows that co-ordination is by no means complete, and that only a small proportion of the substance possesses the cyclic structure.

Formulæ involving singlet linkages have been suggested by D. C. Jones* for associated liquids which account for the

* *J.C.S.*, 1928, 1196.

parachor anomaly, but are open to criticism on other grounds. Thus, following Hantzsch, Jones suggests for the double molecule of the acids formula IV, which gives three shared



IV

electrons to the hydrogen atoms. This is contrary to Pauli's principle (cf. p. 70), and also makes the hydrogen atoms negative and the oxygen atoms attached to them positive.

Water and inorganic acids which contain a free hydroxyl group show a similar anomaly; the halogen acids appear, however, to be normal liquids (table 68).

TABLE 68

Water and Inorganic Acids

Water.[1]			*Nitric Acid.*[2]			*Sulphuric Acid.*[3]		
[*P.*] *calc.* 54·2			[*P.*] *calc.* 111·2			[*P.*] *calc.* 159·2		
t.	[*P.*]*obs.*	*Anomaly.*	*t.*	[*P.*]*obs.*	*Anomaly.*	*t.*	[*P.*]*obs.*	*Anomaly.*
0	53·1	−1·1	11·6	104·4	−6·8	10·2	144·8	−14·4
20	52·7	−1·5	46·2	105·0	−6·2	46·4	146·9	−12·3
40	52·4	−1·8	78·2	105·7	−5·5	78·5	148·4	−10·3
60	52·3	−1·9				132·5	152·3	−6·9
80	52·2	−2·0				*Halogen Acids.*[4]		
100	52·1	−2·1		*Acid.*		[*P.*] *obs.*	[*P.*] *calc.*	*Anomaly.*
120	52·1	−2·1		HCl		67·8	71·4	−3·6
130	52·0	−2·2		HBr		85·4	85·1	0·3
				HI		105·3	108·1	−2·8

[1] Int. Crit. Tables, IV, 447.
[2] Aston and Ramsay, *J.C.S.*, 1894, **65**, 170.
[3] Walden, *Z. f. physikal. Chem.*, 1908, **65**, 129.
[4] Steele, McIntosh, and Archibald, *ibid.*, 1906, **55**, 145.

The anomaly for water is very small and appears to increase as the temperature rises.

A similar behaviour is shown by the lower members of the series of primary and secondary amines, in which the NH group probably plays the same part as the OH group in the alcohols. The parachors in table 69 are calculated from the observations of Jaeger.* It will be seen that the tertiary amine, except at

* *Z. f. anorgan. Chem.*, 1917, **101**, 1.

TABLE 69

Primary, Secondary, and Tertiary Amines

Methylamine. [*P.*] *calc.* 102·8			*Dimethylamine.* [*P.*] *calc.* 141·8			*Trimethylamine.* [*P.*] *calc.* 180·8		
t.	[*P.*]*obs.*	*Anomaly.*	*t.*	[*P.*]*obs.*	*Anomaly.*	*t.*	[*P.*]*obs.*	*Anomaly.*
−70	95·1	−7·7	−78	133·4	−8·4	−73	176·3	−4·5
−49	96·2	−6·6	−50	134·1	−7·7	−52	175·0	−5·8
−20	96·8	−6·0	−23	135·3	−6·5	−32	178·9	−1·9
−12	95·5	−7·3	0	136·6	−5·2	−19	179·6	−1·2
			+5	136·6	−5·2	−4	178·3	−2·5

the lowest temperatures where the experimental errors are probably greatest, shows a much smaller anomaly than mono- and dimethylamine. Ammonia, like water, gives a parachor which is nearly normal: [*P.*] *obs.* = 60·7, whilst [*P.*] *calc.* = 63·8.

Some Anomalies in Simple Molecules

It is convenient at this point to call attention to a number of parachor anomalies which have been found in simple molecules, and which can be accounted for in a somewhat similar manner to that suggested for associated liquids. Seven examples of this type of anomaly have been encountered, and are collected in table 70; the table also gives the parachors of a number of equally simple substances which behave normally. It is evident from the latter group that the additive character of the parachor is maintained even for substances containing two and three atoms in the molecule.

TABLE 70

Anomalies in Simple Molecules

Abnormal Substances.					*Normal Substances.*			
Substance.	*Observer.*	[*P.*] *obs.*	[*P.*]*calc.*	*Anomaly.*	*Substance.*	[*P.*] *obs.*	[*P.*]*calc.*	*D*
N_2	B. & D.	60·4	71·4	−11·0	H_2	35·2	34·2	+
O_2	,,	54·0	63·2	−9·2	Cl_2	111·5	108·3	+
N_2O	G.	81·1	89·8	−8·7	Br_2	132·1	136·0	−
CO	B. & D.	61·6	(a) 48·0	+13·6	H_2O	52·4	54·2	−
			(b) 69·6	−8·0				
CO_2	Q.	77·5	91·2	−13·7	HCN	81·5	81·0	+
SO_2	G.	101·5	109·8	−8·3	CS_2	144·1	147·6	−
SO_3	Sch. Ber.	103·6	128·2	−24·6	NOCl	108·1	111·0	−

For full references see p. 190.

For nitrogen and oxygen the surface tensions found by Baly and Donnan have been confirmed by observations in the Leiden laboratories, so that the anomalies cannot be ascribed

to experimental errors. Since nitrogen and oxygen are the elements which are present in the characteristic groups of associated liquids (OH and NH_2), it seems possible that the free elements themselves are associated, and that the liquid contains aggregates composed of two or more simple molecules held together by means of singlet linkages, e.g. V. The parachor per O_2 molecule calculated for this structure is 43·0; hence, on this hypothesis, liquid oxygen contains about 45% by weight of triple molecules. A similar explanation may be given of the negative anomalies found for N_2, N_2O, CO_2, and SO_2. It is noteworthy that whilst CO_2 shows a marked negative anomaly, CS_2 gives a much smaller anomaly and is classified as normal.

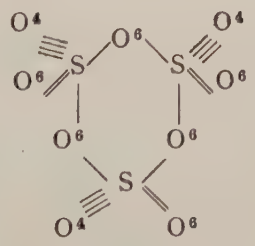
V

The parachor of carbon monoxide is of special interest. If the carbon atom in this substance is divalent, the electronic formula VI is obtained, corresponding to a parachor of 48·0. It is possible, however, to complete the octet on each atom by the sharing of six electrons as in VII, which corresponds to a parachor of 69·6. The observed figure, 61·6, is much larger than the value expected for VI, and it appears that this substance is essentially VII, but that some association occurs and gives a lower value to the parachor. It seems probable that other compounds in which divalent carbon is present will prove to have similar structures with completed octets. Thus the isonitriles are probably represented by the electronic formula VIII.

VI

VII

VIII

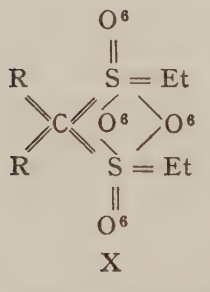


IX

The parachor found for SO_3, from the measurements of two independent observers, shows a large anomaly of $-24{\cdot}6$. The general behaviour of liquid SO_3 is that of a highly associated liquid, and this figure is very close to the value calculated for complete association into triple molecules IX, for which an anomaly of $-21{\cdot}2$ per SO_3 molecule is predicted. This interpretation of the experimental data is supported by the anomalies found for the disulphones, sulphonal, and trional.* These substances have the general formula $R_2C(SO_2Et)_2$; they are stable crystalline solids which can be readily purified and measured, yet their parachors show a large negative anomaly.

	[*P.*] *obs.*	[*P.*] *calc.*	*Anomaly.*
Sulphonal, $Me_2C(SO_2Et)_2$	465·5	477·2	−11·7
Trional, $MeEtC(SO_2Et)_2$	493·8	516·2	−22·4

The molecular weights of these substances in solution are normal, so that the anomaly cannot be ascribed to association in the usual sense of the term. It is possible, however, to account for these negative anomalies by postulating an interaction between the two SO_2 groups of a similar type to that which is supposed to occur between similar groups in separate molecules in SO_3, etc., giving a cyclic structure involving singlet linkages, X. Here, as in the structure suggested for SO_3, it is the oxygen atoms held originally by a semipolar double bond which are supposed to form a bridge by means of singlet linkages. This behaviour has so far been found only in the β-disulphones. γ and δ-disulphones, in which two and three carbon atoms are interposed between the SO_2 groups, as well as a large number of substances containing only one SO_2 group, all give normal parachors.



X

Conducting Liquids. (1) Fused Metals

The second group of liquids, namely, those which are good conductors of electricity, usually show anomalies in physical properties which are probably connected with the presence of a high concentration of electrically charged particles. The

* Freiman and Sugden, *J.C.S.*, 1928, 263.

general tests for association give very conflicting results. The specific heat ratio Cp/Cv and the vapour densities of the alkali metals, silver, zinc, cadmium, mercury, and thallium, show that the vapours of these metals consist of monatomic molecules; a small degree of association is found by these methods for lead, antimony, and bismuth. Similarly Hildebrand's latent heat method gives monatomic molecules in the liquid state for zinc, cadmium, and mercury. The Ramsay-Shields constants for metals are very low and even negative, and cannot, therefore, be used to calculate the degree of association. Walden's formula at the freezing point gives sodium, potassium, tin, and lead as monatomic, but the validity of this method is somewhat doubtful. The study of the molecular weights of metals in solution in each other is complicated by the frequent occurrence of solid solutions and intermetallic compounds. Extensive series of measurements have been made by Ramsay,* who used mercury as solvent, and by Heycock and Neville,† who also studied the depression of the freezing point of tin by other metals. In both series the dissolved metal was usually found to be monatomic, but evidence of association was obtained with tin, lead, antimony, bismuth, and aluminium.

If the results of the surface tension methods of detecting association are neglected, it seems probable that the metals of groups I and II of the periodic table are monatomic in the liquid state, whilst the metals of groups III, IV, and V may be associated. The remaining metals belong to the transition series, and the free elements have probably not more than two electrons in the outermost energy level; they would, therefore, be expected to behave like the metals of the first two groups. The scanty evidence available for these elements indicates that they are monatomic in accordance with this view.

The surface tensions and densities of a number of metals have been measured, and the parachors calculated from these data are collected in table 71. It must be remembered that the measurement of the physical properties of fused metals presents great experimental difficulties, and some of the data quoted in the table may be burdened with large experimental

* *J.C.S.*, 1889, **55**, 521.

† *Proc. Chem. Soc.*, 1889, **5**, 41; *J.C.S.*, 1889, **55**, 666; *ibid.*, 1890, **57**, 376.

errors. For mercury, tin, antimony, bismuth, and lead independent values of the atomic parachors have been determined by measurements on covalent compounds of these elements, and are given under [P] at. in the table. It will be seen that whilst mercury is monatomic, the other metals, all of which happen to belong to groups III, IV, or V of the periodic table, show a definite positive anomaly. These positive anomalies can be accounted for by the formation of molecules of the metals by means of double or triple bonds. If a double bond joins two atoms, the parachor (calculated for one atom) will show a positive anomaly of 11·6 units, whilst the presence of a triple bond would give twice this anomaly. The parachors of aluminium, lead, antimony, and bismuth

TABLE 71

Parachors of Fused Metals

Metal.	*Observer.**	[*P*] *obs.*	[*P*] *at.*	*Anomaly.*
Mercury	Smith	68·0	68·7	−0·7
	H. & E.	69·0		+0·3
	H.	69·4		+0·7
	Brown	69·4		+0·7
Aluminium	Smith	55·0	38·6	+16·4
Tin	Smith	83·4	54·8	+28·6
	H	81·8		
	B.	83·8		+29·0
	S. & D.	86·8		+32·0
Lead	Smith	(114·2)	76·2	(+38·0)
	H.	89·3		+13·1
	B.	91·5		+15·3
	D. & S.	93·5		+17·3
Antimony	Smith	76·8	66·0	+10·8
	B.	82·0		+16·0
	D. & S.	83·9		+17·9
Bismuth	H.	92·0	80·0	+12·0
	B.	94·4		+14·4

* For references see p. 190.

would seem to indicate that these metals consist of molecules containing two atoms which share four electrons, whilst with tin six electrons are shared by two tin atoms. These characteristic positive anomalies are also found in certain fused salts

(p. 178), and can again be explained by the presence of multiple bonds. It must be remembered that both series of substances are highly anomalous in their physical properties, and the parachor anomaly may only be another manifestation of the factors which bring about electrical conductivity. On the other hand, the fact that mercury and certain fused salts give normal parachors lends support to the explanation of these anomalies in terms of structure.

The parachors of metallic copper, silver, gold, zinc, cadmium, and gallium cannot at present be compared with atomic parachors deduced from covalent compounds of these elements. It seems probable, however, that these metals are monatomic, and the observed parachors are equal to the atomic constants. This conclusion is supported by the fact that the observed parachors lie smoothly on the atomic number—atomic parachor curve (p. 183).

Conducting Liquids. (2) Fused Salts

The physical properties of salts in the liquid state closely resemble those of fused metals. Their vapour densities usually show little indication of association ; the few salts which give abnormally high values are AgCl, $SnCl_2$, $FeCl_2$, $InCl_2$, and $GaCl_3$. Al_2Cl_6, Fe_2Cl_6, and the corresponding bromides and iodides give vapour densities corresponding to these formulæ ; these substances should not be classed as salts, for they have a negligibly small electrical conductivity in the fused state. The structure of Al_2Br_6 has already been discussed (p. 148), and the other halides have probably a similar constitution.

The molecular weights found for salts in solution fall into two groups. In suitable dissociating solvents low values are found and are readily accounted for by electrolytic dissociation. Salts are usually insoluble or sparingly soluble in solvents of low dielectric constant, e.g. benzene and chloroform, but certain salts, notably the alkyl ammonium halides, are soluble in such solvents and then give abnormally high molecular weights. Some examples of this behaviour are given in table 72, which is abstracted from the large number of investigations on such systems carried out by Turner and his co-workers.* It is probable that these solutions, and the

* Turner, *J.C.S.*, 1911, **99**, 880 ; Turner and Pollard, *ibid.*, 1914, **105**, 1751.

TABLE 72

Abnormal Molecular Weights of Dissolved Salts.

Chloroform Solutions.		*Influence of Solvent on the Molecular Weight of $(C_3H_7)_4NI$.*	
Salt.	*Degree of Association.*	*Solvent.*	*Degree of Association.*
$C_3H_7NH_3Cl$	4·6 — 6·2	Water	0·49 — 0·71
$(C_3H_7)_2NH_2Cl$	2·0 — 2·3	Ethyl alcohol	0·92 — 1·04
$(C_3H_7)_4NCl$	2·3 — 3·2	Amyl alcohol	1·6 — 2·2
$(C_3H_7)_4NBr$	2·9 — 3·8	Chloroform	4·0 — 4·4
$(C_3H_7)_4NI$	4·0 — 4·4	Diphenylamine	4·1 — 4·4

similar solutions of tetra-amyl ammonium iodide in solvents of low dielectric constant for which Walden found anomalous conductivity-concentration curves, all contain colloidal aggregates and resemble the soap solutions described in an earlier section (p. 164).*

Simple inorganic salts usually give in solution normal molecular weights or exhibit electrolytic dissociation. Slight indications of association are found for stannous chloride dissolved in pyridine, and more markedly for cobalt and cupric chlorides in urethane, silver chloride, bromide and iodide in piperidine, and certain ammonium salts in liquid sulphur dioxide. The Ramsay-Shields and Walden constants of fused salts are usually very low ; some examples are given in table 60 (p. 159), but it is very doubtful whether any significance can be attached to these figures.

The surface tensions and densities of a large number of fused salts are recorded in chemical literature, and the parachors calculated from these observations are conveniently considered under three headings. We shall discuss first the data for salts of organic bases, next the salts of metals whose atomic parachors are known, and finally salts of metals for which the atomic parachor has not yet been determined from covalent compounds.

All the available data for salts of organic bases are collected in table 73 ; in computing the value of [P.] calc. in this table the value of the polar bond has been taken as — 1·6. With the exception of substances 5, 9, and 10, the agreement between the observed and calculated parachors is as good as could be

* Cf. Lowry, *Phil. Mag.*, 1928 [7], **5**, 1076.

expected. Most of these substances are very hygroscopic and very soluble in water; in consequence it is difficult to obtain pure specimens for examination. It seems very probable that the result for ethyl ammonium nitrate, which is a liquid at room temperature, is due to incomplete purification, since its isomeride, dimethyl ammonium nitrate, gives a normal parachor.* The isoamyl derivatives also show large and irregular variations which require further investigation.

TABLE 73

Salts of Organic Bases

No.	*Substance.*	*Observer.*	[*P.*] *obs.*	[*P.*] *calc.*	*Diff.*
1	Methylaniline hydrochloride	S. & W.	348·5	345·5	+3·0
2	Ethylaniline hydrochloride	,,	381·9	384·5	−2·6
3	Tetrapropylammonium picrate	,,	932·2	928·3	+3·9
4	Dimethylaniline hydrogen sulphate	,,	469·9	472·5	−2·6
5	Ethylammonium nitrate	W.	234·9	251·4	−16·5
6	Dimethylammonium nitrate	,,	249·7	251·4	−1·7
7	Diethylammonium nitrate	,,	324·8	329·4	−4·6
8	Dimethylaniline hydrobromide	,,	406·3	398·2	+8·1
9	Tri-*iso*amylammonium thiocyanate	,,	761·6	776·4	−14·8
10	Tetra-*iso*amylammonium iodide	,,	895·5	950·3	−54·8

These substances are of interest, since they are salts for which all the atomic parachors are known with certainty. An extensive investigation of the electrical conductivity, viscosity, and density of molten picrates of organic bases has recently been carried out by Walden, Ulich, and Birr,† who conclude that whilst the salts of primary, secondary, and tertiary bases are only partially ionised, the quaternary salts are completely ionised in the fused state. The parachor of tetrapropylammonium picrate agrees within the limits set by the experimental error with the calculated value, so that in this salt the value deduced for the polar bond from that of the semipolar double bond, namely, − 1·6, is satisfactorily confirmed. This raises, however, another problem as to the structure of the unionised part of the salts of primary, secondary, and tertiary bases. The anion could not be linked to nitrogen by a covalency without violating the octet rule; a structure with

* Since this was written Walden's result has been confirmed by the writer.

† *Z. f. physikal. Chem.*, 1927, **131**, 1, 21, 31.

two singlet linkages could be written similar to that for PCl_5, but this would give a negative anomaly in the parachor and most of the parachors are normal. The conductivity method of estimating degree of dissociation is of course open to grave criticism, particularly with systems containing a high volume concentration of ions, and in fused salts the electrostriction effects discussed in Debye and Huckel's theory of strong electrolytes will have a very large influence upon the conductivity. Large negative and positive parachor anomalies are found in some of the substances discussed in the following sections of this chapter, and indicate that fused salts are very complex systems. Much more definite evidence is needed as to the constitution of these systems, and particularly as to the proportion of neutral and charged molecules, so that fused salts offer a very promising field for further investigation.

Passing to the second group, the atomic parachors of thallium, tin, and lead are known with fair accuracy, and the parachors of salts of these metals are collected in table 74. To these are added certain silver salts for which the atomic parachor given by the fused metal is used in calculating the value of [P.] calc. In all cases the polar bond is allotted the value $-1{\cdot}6$.

TABLE 74

Parachors of Fused Salts

Substance.	*Observer.*	[*P.*] *obs.*	[*P.*] *calc.*	*Anomaly.*
Thallous formate	S.	150·3	144·3	+6·0
Thallous acetate	S.	183·5	183·3	+0·2
Thallous nitrate	J.	180·7	156·5	+24·2
	S.	177·3	156·5	+20·8
Stannous chloride	J.	183·8	160·2	+23·6
Lead chloride	L. & K.	194·5	181·6	+12·9
Silver chloride	L. L. & H.	98·8	114·5	−15·7
Silver nitrate	J.	157·2	154·3	−2·9

Tl = 64·0, Sn = 54·8, Pb = 76·2, Ag = 61·8

The most noteworthy feature of these results is the large positive anomaly found for thallous nitrate and stannous chloride. The presence of ions, e.g. $Sn \equiv Sn$, would give an anomaly of + 11·6, but the anomalies found are much larger. Here triple bonds cannot be assumed, since the ions do not possess enough valency electrons to form them.

TABLE 75

Salts of the Alkali Metals

Salt.	*Temp.*	*Parachor.*	*Mean [P.]*	*Σ [P.]*	*Atomic Parachor.*
LiF	850–1000	57·8–59·3	58·5	24·1	34·4
LiCl	600–775	97·2–99·6	98·4	52·7	45·7
$LiNO_3$	350–500	130·0–132·9	131·5	91·5	40·0
Li_2SO_4	860–1150	212·4–220·6	216·0	121·8	47·1×2
NaF	1010–1190	81·5–83·9	82·7	24·1	58·6
NaCl	800–900	123·4–126·7	124·8	52·7	72·1
NaBr	760–900	142·2–145·4	143·8	66·4	77·4
NaI	700–750	169·4–171·3	170·8	89·4	81·4
$NaNO_3$	320–600	147·9–158·4	152·9	91·5	61·4
$NaPO_3$	800–1100	175·4–181·7	178·1	117·7	60·4
Na_2SO_4	900–1100	257·5–265·8	261·1	121·8	69·6×2
KF	900–1100	106·7–111·0	109·0	24·1	84·9
KCl	800–900	154·6–158·4	156·6	52·7	103·9
KBr	775–825	173·6–175·1	174·3	66·4	107·9
KI	737–812	204·3–206·8	205·2	89·4	115·8
KNO_3	380–580	184·2–193·6	189·0	91·5	97·5
KPO_3	900–1200	201·4–207·0	204·4	117·7	86·7
K_2SO_4	1070–1350	319·5–336·5	328·0	121·8	103·1×2
RbF	800–1040	121·2–125·9	123·1	24·1	99·0
RbCl	750–880	181·0–185·0	182·8	52·7	130·0
RbBr	730–830	190·5–195·0	192·7	66·4	126·3
RbI	670–820	224·3–229·5	226·8	89·4	137·4
$RbNO_3$	320–580	192·5–203·7	197·9	91·5	106·4
Rb_2SO_4	1080–1350	356·9–368·1	361·8	121·8	120·0×2
CsF	720–880	135·4–138·6	136·9	24·1	112·8
CsCl	660–770	186·6–190·7	188·7	52·7	136·0
CsBr	650–750	205·2–209·2	207·5	66·4	141·1
CsI	650–770	239·8–245·0	242·4	89·4	153·0
$CsNO_3$	425–575	215·7–221·2	218·0	91·5	126·5
Cs_2SO_4	1030–1220	386·8–393·1	388·8	121·8	133·5×2

Approximate atomic parachors

Li = 50, Na = 80, K = 110, Rb = 130, Cs = 150

Finally, we have to deal with a large number of observations on the surface tensions of fused salts of the alkali metals, nearly all due to Jaeger.* These are summarised in table 75 and are used to obtain rough values for the atomic parachors of these elements. Jaeger's surface tension observations usually cover a larger temperature range than his density measurements; to avoid errors due to extrapolation of the density-temperature formulæ, the parachors are calculated only for the range of temperatures for which these formulæ are valid. Even within these limits the parachors show a considerable variation, and usually increase with rising temperature. The amount of this variation is indicated in the third column of the table whilst the mean parachor is given in the fourth column. From this is subtracted the sum of the appropriate constants for the anion to give the atomic parachor in the last column.

From a survey of the data collected in this table it will be seen that the bromides and iodides usually give the highest values for the atomic parachors, whilst the nitrates and sulphates, and particularly the fluorides, give much lower figures. It is evident that large negative anomalies must occur in the fluorides, etc., which are much larger than those found with associated organic liquids. The only independent evidence at present available for the atomic parachors is the recent determination of the surface tension of sodium by Poindexter† which gives Na = 97·4. This is much higher than any of the values given by the sodium salts, and requires confirmation. Until further determinations have been made of the atomic parachors it would obviously be useless to speculate about the constitution of these salts. Meanwhile, rough values of the atomic parachors of the metals can be deduced from the data for the higher halides, and are given below the table.

* *Z. f. anorgan. Chem.*, 1917, **101**, 1.
† *Physical. Rev.*, 1926 [2], **27**, 820.

CHAPTER IX

ATOMIC PARACHORS AND ATOMIC NUMBER

In the course of the investigations described in earlier chapters the atomic constants for 44 of the 92 chemical elements have been determined. These are set out in alphabetical order in table 76. The values in brackets are rough values only, and may be in error by ± 10 units ; those marked with an asterisk

TABLE 76

Atomic Parachors

Element.	*Symbol.*	[*P.*]	*Element.*	*Symbol.*	[*P.*]
Aluminium	Al	38·6*	Lead	Pb	76·2*
Antimony	Sb	66·0	Lithium	Li	(50)
Argon	A	54·0	Mercury	Hg	69·0
Arsenic	As	50·1	Molybdenum	Mo	(80)
Barium	Ba	(106)	Neon	Ne	25·0
Beryllium	Be	37·8*	Nickel	Ni	(50)
Bismuth	Bi	80*	Nitrogen	N	12·5
Boron	B	16·4	Osmium	Os	80·4*
Bromine	Br	68·0	Oxygen	O	20·0
Cadmium	Cd	(70)	Phosphorus	P	37·7
Cæsium	Cs	(150)	Potassium	K	(110)
Calcium	Ca	(68)	Rubidium	Rb	(130)
Carbon	C	4·8	Selenium	Se	62·5
Chlorine	Cl	54·3	Silicon	Si	25·0
Chromium	Cr	54·0*	Silver	Ag	63*
Copper	Cu	(46)	Sodium	Na	(80)
Fluorine	F	25·7	Sulphur	S	48·2
Gallium	Ga	50*	Thallium	Tl	64*
Gold	Au	61*	Tin	Sn	57·9
Helium	He	20·5	Titanium	Ti	45·3*
Hydrogen	H	17·1	Tungsten	W	(90)
Iodine	I	91·0	Zinc	Zn	50·7*

are based on observations on a few substances only, and may be in error by ± 3 units. The remainder are probably correct to the nearest unit. The observations from which these constants are derived are summarised on pages 186 ff.

Periodic Variation of Atomic Parachor with Atomic Number

Since the parachor is a measure of the molecular volume, corrected for the influence of internal pressure, the atomic constants should give corrected atomic volumes provided that the assumptions made in deducing these constants from the molecular parachors are correct. In most cases the only hypothesis involved is the adoption of the value zero for the contribution of the single chemical bond, or (cf. p. 110) the equivalent hypothesis that shared and unshared electrons make the same contribution to the parachor. A direct test of this hypothesis is given by the mercury and thallium compounds discussed on page 111, and further indirect evidence is supplied by the regularities in the curve of atomic parachors plotted against atomic numbers shown in fig. 11. This curve shows a close resemblance to Lothar Meyer's well-known curve of atomic volumes ; hence the atomic parachors appear to measure a real property of the atom and no serious errors have been introduced in calculating them from the molecular constants.

For the first two short periods the atomic parachors are all known except that of magnesium. The values for the alkali metals are somewhat uncertain, but a considerable increase on the values chosen for these elements would not materially alter the form of the curve. It will be seen that in these two periods there is a steep drop from group I to group IV, followed by a more gradual rise to group VIII. It is noteworthy that, within the limits of the experimental error, there is no change in parachor on passing from fluorine (25·7) to neon (25·0), or from chlorine (54·3) to argon (54·0). The completion of the octet seems, therefore, to be accompanied by a contraction in volume which compensates for the contribution of the added electron.

The constants for most of the elements of the first transition series are known with moderate accuracy. Here the filling of the 3_3 level has very little effect upon the atomic parachor and, from titanium to zinc, the constants all lie between 45 and 54 units. This effect seems to persist up to gallium ; unfortun-

ately no evidence is as yet available for germanium, but there is probably a minimum on the curve for this element after

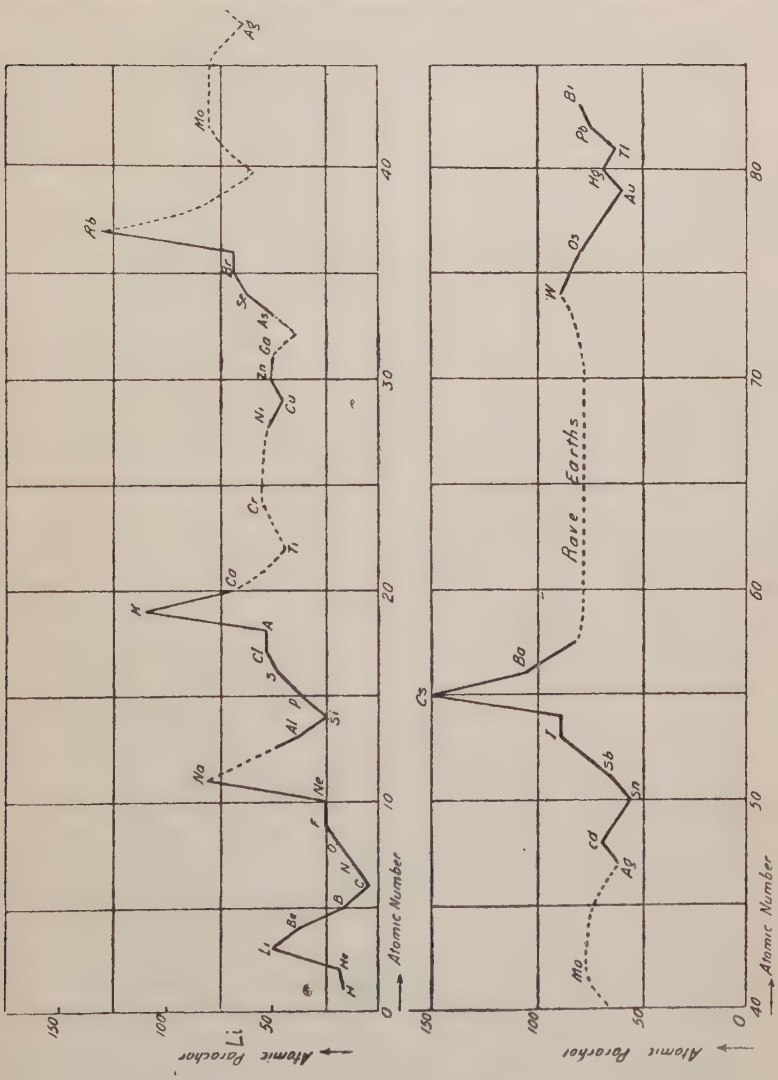


Fig. 11

which the normal rise through arsenic, selenium, and bromine is found.

For elements of atomic number greater than 40 there are

many gaps in the series of atomic parachors, but the available constants are sufficient to indicate the general course of the curve. The second transition series follows the same course as the first, whilst the rare earth elements (for which no parachors are as yet determined) will probably lie on a flat portion of the curve as shown in the figure, and all have atomic parachors in the neighbourhood of 80 units.

A minor feature of the curve which is of interest is the subsidiary minimum found for copper, silver, and gold. These elements stand at the end of a transition series, and mark the completion of the filling of an inner sub-group. The atomic parachors are, however, based on a few measurements only, and other compounds of these elements must be examined before the existence of this minimum can be regarded as proved.

The parachors of most of the elements of groups IV to VII are known, and show a number of interesting relations between the constants for adjacent elements. The parachors are set out in table 77 (omitting the transition elements), and the horizontal and vertical differences for neighbouring elements are tabulated. These differences show marked regularities so that the missing parachors for certain elements can be predicted with a fair degree of accuracy. Thus krypton and xenon will probably have parachors almost identical with those of bromine and iodine, and the constants 36 for germanium and 81 for tellurium seem to be indicated by the differences for neighbouring elements. These predicted figures are bracketed in the table.

A similar scheme can be devised for the elements immediately following copper, silver, and gold, and is shown in table 78. It seems probable that the constant for indium will probably be in the neighbourhood of 69 units. In this series it is remarkable that the addition of successive electrons (and equivalent positive charges on the nucleus) causes very little change in the atomic parachor up to group III, and then gives a sudden fall at group IV. Lead is an exception here and requires further investigation. Another remarkable feature is the small difference between the atomic parachors of corresponding elements in the last two rows of the table, e.g. Ag Au, Cd Hg; the filling up of the 4_4 and 5_3 levels seems to produce little or no change in the volume of the atom.

In the remainder of the periodic table the atomic parachors

TABLE 77

Relations between Atomic Parachors (1)

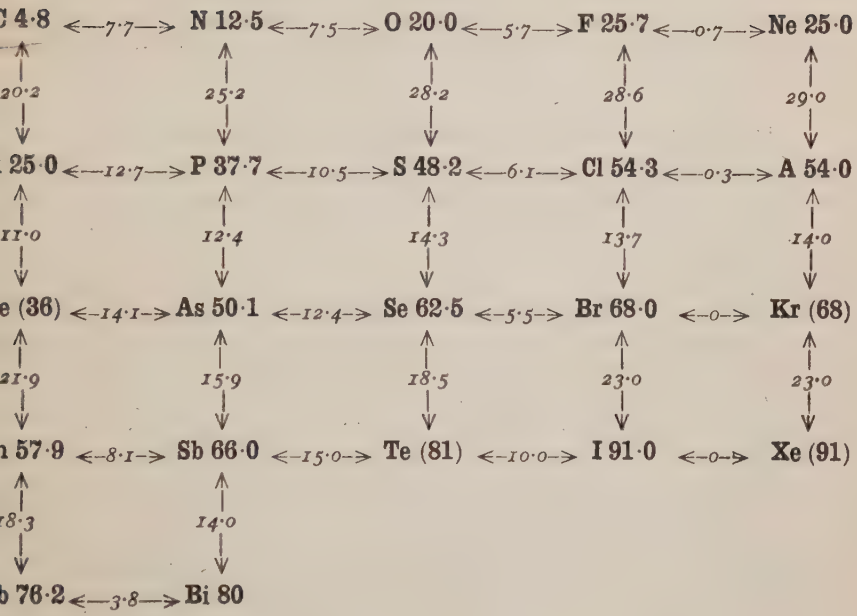
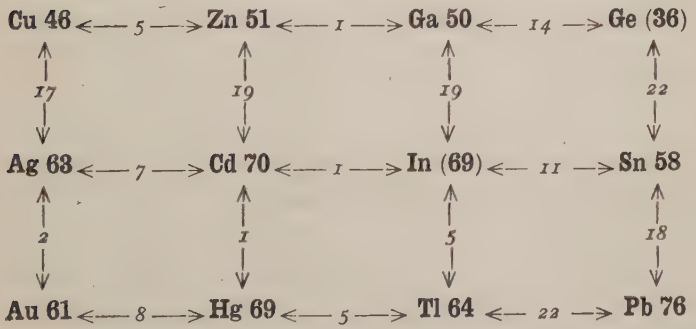


TABLE 78

Relations between Atomic Parachors (2)



known at present are too few in number to attempt to trace any similar relationships; when these constants have been determined it is probable that they will exhibit similar regularities. Fortunately compounds of most metallic elements with β-diketones or similar chelate groups can be prepared, which are fusible without decomposition, and can therefore be used for the determination of the parachor.

Sources from which the Atomic Parachors are Derived

The data on which the atomic parachors are based are summarised below. The elements are grouped in the order of the groups in the periodic table. For full references see page 190.

Group 0. The Inert Gases. The surface tensions and densities in the liquid state of three of these gases have been determined in the Leiden laboratories with the following results.

Substance.	*Observer.*	*Parachor.*
Helium	M.C.O. & S.	20·5
Neon	U. K. & N.	25·0
Argon	B. & D.	54·0

Group I (a). The Alkali Metals. From the evidence discussed in chapter VIII the following provisional values are adopted.

Li.	*Na.*	*K.*	*Rb.*	*Cs.*
50	80	110	130	150

These may be in error by at least ± 10 units.

Group I (b). The Noble Elements.

Substance.	*Observer.*	[*P.*] *obs.*	Σ [*P.*]	*Atomic Parachor.*
Copper	Smith	44·8	0	44·8
,,	D. & S.	47·0	0	47·0
			Mean	46
Silver	Smith	61·8	0	61·8
Silver chloride	L. L. & H.	98·8	52·7	(46·1)
Silver nitrate	J.	157·2	92·5	64·7
		Mean (neglecting chloride)		= 63
Gold	Smith	60·6	0	60·6

Group II.

Beryllium from its co-ordinated compounds = 37·8 (p. 145).

Substance.	*Observer.*	[*P.*] *obs.*	Σ [*P.*]	*Atomic Parachor.*
Calcium chloride	M.	177	109	68
Barium chloride	M.	215	109	106
Zinc	Smith	58·0	0	(58·0)
	B.	50·7	0	50·7
Cadmium	B.	70·0	0	70·0
Mercury	Smith	68·0	0	(68·0)
	H. & E.	69·0	0	69·0
	H.	69·4	0	69·4
	Brown	69·4	0	69·4
Mercury diphenyl	C. & S.	448·7	380·0	68·7
			Mean	69·2

Group III. Boron.

Substance.	*Observer.*	[*P.*] *obs.*	Σ [*P.*]	*Boron.*
Boron trichloride	M. & R.	178·8	162·9	15·9
Methyl borate	E. & S.	243·7	228·3	15·4
Ethyl borate	,,	363·1	345·3	17·8
			Mean	16·4

Aluminium: from co-ordinated compounds Al = 38·6 (p. 147).
Gallium: from the fused metal (R. & B.) Ga = 50·0.
Thallium: from co-ordinated compounds and salts Tl = 64 (p. 145).

Group IV. From organic compounds C = 4·8.

Substance.	*Observer.*	[*P.*] *obs.*	Σ [*P.*]	*Atomic Parachor.*
Silicon tetrachloride	R. & S.	229·2	217·2	(12·0)
,, ,,	M. & R.	242·2	217·2	25·0
	The higher value is more probable.			
Titanium tetrachloride	G. & S.	262·5	217·2	45·3
Stannic chloride	,,	272·8	217·2	55·6
Stannic bromide	,,	329·3	272·0	57·3
Tin tetraethyl	,,	441·1	380·4	60·7
			Mean	57·9
Lead tetraethyl	S.	456·6	380·4	76·2

(Cf. also pp. 174 ff., for data for free metals and salts.)

Group V. From organic compounds N = 12·5.

Phosphorus.

Substance.	*Observer.*	[*P.*] *obs.*	Σ [*P.*]	*Atomic Parachor.*
PCl_3	M. & D.	199·0	162·9	36·1
,,	R. & S.	201·1	162·9	38·2
PBr_3	S. R. & W.	242·9	204·0	38·9
$P(C_6H_5)_3$	W. & S.	607·7	570·0	37·7
			Mean	37·7

Arsenic.

Substance.	*Observer.*	[*P.*] *obs.*	Σ [*P.*]	*Atomic Parachor.*
$AsCl_3$	J.	212·0	162·9	49·1
$AsBr_3$	J.	253·5	204·0	49·5
$PhAsCl_2$	H. & S.	348·3	298·6	49·7
Ph_2AsCl	,,	487·1	434·3	52·8
			Mean	50·3

Antimony.

Substance.	*Observer.*	[*P.*] *obs.*	Σ [*P.*]	*Atomic Parachor.*
$SbCl_3$	F. & S.	227·4	162·9	64·5
$SbPh_3$	W. & S.	637·4	570·0	67·4
			Mean	66·0

Bismuth.

Substance.	*Observer.*	[*P.*] *obs.*	Σ [*P.*]	*Atomic Parachor.*
$BiCl_3$	J.	236·3	162·9	73·4
$BiBr_3$	J.	283·9	204·0	79·9

The higher value seems more probable, hence Bi = c. 80

Group VI. From organic compounds O = 20·0.

Sulphur.

Substance.	*Observer.*	[*P.*] *obs.*	Σ [*P.*]	*Atomic Parachor.*
S_2Cl_2	R. & S.	205·1	108·6	48·2
CS_2	,,	144·7	51·2	46·8
CS_2	M. & T. / M. & D.	143·6	51·2	46·2
CS_2	H.C. & R.	142·9	51·2	45·9
C_2H_5SH	M. & C.	162·9	112·2	50·7
C_6H_5SH	W. & S.	257·5	207·1	50·4
	M. & C.	256·4	207·1	49·2
			Mean	48·2

Chromium: Cr = 54·3 (p. 126).
Selenium: Se = 62·5 (p. 126).

Molybdenum and Tungsten.

Very rough values for these elements can be obtained from Jaeger's measurements on fused sulphates, molybdates, and tungstates in the following manner.

	[*P.*] *obs.*		[*P.*] *obs.*
Na_2MoO_4	288	K_2MoO_4	367
Na_2SO_4	261	K_2SO_4	328
Diff. Mo — S	= 27	Diff. Mo — S	= 39
S	= 48	S	= 48
Mo	= 75	Mo	= 87

Mean Mo = 81

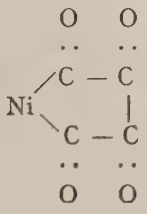
	[*P.*] *obs.*		[*P.*] *obs.*
Na_2WO_4	300	K_2WO_4	373
Na_2SO_4	261	K_2SO_4	328
Diff. W — S	= 39	Diff. W — S	= 45
S	= 48	S	= 48
W	= 87	W	= 93

Mean W = 90

Group VII. From organic compounds F = 25·7, Cl = 54·3, Br = 68·0, I = 91·0.

Group VIII. For nickel carbonyl the measurements of Ramsay and Shields give [*P.*] obs. = 250·8. Assuming that the carbonyl has the

cyclic structure



then $\Sigma[P.]$=200·5 and Ni=50·3.

This structure gives a reasonable value for nickel, and can readily be formulated electronically. The centric structure is difficult to formulate electronically, and does not give a reasonable parachor for nickel. Independent determinations of the constant for nickel (e.g. in its fusible co-ordination compounds) are needed to confirm or exclude this structure for the carbonyls.

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CHAPTER X

THE QUANTUM THEORY OF SHARED ELECTRONS

Wave-Mechanics and Molecular Structure

The conception of shared electrons due to G. N. Lewis is the most characteristic feature of modern electronic theories of valency, and is mainly responsible for the large degree of success which these theories have attained. For some time this conception has been based chiefly on chemical evidence, but during the last two years the development of the quantum theory has given an interpretation of the linkage composed of shared electrons in terms of quantum numbers which is of fundamental significance. In this chapter an attempt will be made to outline the results which have been obtained by the application of the methods of wave-mechanics to the problem of molecular structure. The mathematical treatment is very complex and will not be discussed, but the conclusions reached are of fundamental importance for chemistry and give physical significance to the chemist's conception of shared electrons.

This advance is due to the new mathematical weapon of the wave-mechanics developed by de Broglie, Schroedinger, and others. It has long been known that in many of the problems of optics it is immaterial whether we regard a ray of light as a train of waves, or as a stream of particles possessing mass and velocity ; these two methods of treating optical problems lead to exactly the same results so long as the dimensions of the obstacles which affect the path of the ray are large compared with the wave-length of the light. When, however, the dimensions become comparable in size with the wave-length, the problem must be treated by wave methods and the particle method breaks down. Thus, at the beginning of last century, the phenomena of diffraction and interference, which can only be accounted for on the wave theory, led to the abandonment of Newton's particle theory of light.

A similar argument has been developed to account for the failure of classical mechanics when problems dealing with dimensions as small as those of atoms and molecules are concerned. Schroedinger suggests that instead of regarding an atom as an assemblage of particles, it should be regarded as a source of waves. Instead of an electron moving in an orbit he postulates an emission of fundamental waves, termed ϕ-waves, which are not identical with ordinary light. If an atom is simultaneously emitting two sets of ϕ-waves which are of different frequency, these will give beats, and it is the beats which are identified with the radiation emitted by an atom. A loose analogy can be drawn between such a process and a familiar phenomenon in wireless reception. The ϕ-waves correspond to the carrier waves, and the observed radiation from an atom is represented by the heterodyne whistle, or beat note, produced by the interference of two carrier waves of nearly the same frequency. The analogy must not be pushed too far; thus the ϕ-waves in Schroedinger's theory have some remarkable properties, and are supposed to be transmitted with a much higher velocity than that of their beat notes.

Such a theory may seem at first sight unnecessarily complex, but it has achieved some remarkable successes in reconciling the classical theory of dynamics which holds for large-scale phenomena and the quantum theory which holds for atomic and molecular dimensions. In fact, the characteristic quantum numbers are given quite naturally by the wave-mechanics theory, and turn out to be the constants which define the solutions of the differential equation for the atom model. The principal and azimuthal quantum numbers are readily accounted for in this fashion, but the development of the theory has not yet progressed far enough to incorporate the conception of the spinning electron in a completely satisfactory manner without introducing new hypotheses. At present, therefore, the wave-mechanics can be accepted as a mathematical weapon which is peculiarly well adapted for dealing with problems of atomic structure, and the question of the truth of its physical basis can be left undecided.* We need not concern ourselves as to whether the electron really is a charged

* Eddington (*The Nature of the Physical World*, Camb. Univ. Press, 1928, p. 219) comments, "Schroedinger's wave-mechanics is not a physical theory, but a dodge—and a very good dodge too."

particle moving in an orbit, or is a train of waves of a peculiar type ; the results of the wave-mechanics analysis of a problem are invariably translated back into terms of the more familiar electronic model in order to appreciate their significance, so that this model still remains as the most convenient mental picture of the structure of atoms and molecules.

In the older quantum theory the energy levels in an atom could be defined experimentally if radiation of a known frequency was emitted, but the prediction of energy levels and the discussion of the stability of systems containing more than one nucleus, i.e. molecules, presented grave difficulties. On the wave-mechanics theory the problem becomes one of the interference of trains of waves, and in simple cases has yielded results which appear to be of great importance for chemistry and which support strongly the conception of shared electrons.

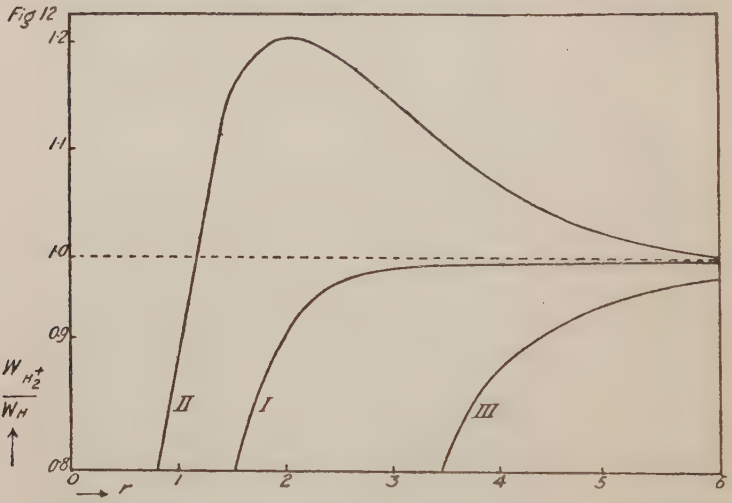
Structure of H_2^+ and H_2

The simplest case to consider is that of the hydrogen molecule ion H_2^+, which is found commonly in positive ray experiments and gives rise to characteristic band spectra. The average life of this molecule is estimated at about 0·02 seconds, which is very long compared with those of atoms in the excited states associated with the production of line spectra (about 10^{-8} seconds), so that it must have a stability comparable with that of chemical molecules. This molecule consists of two hydrogen nuclei and one electron, and its structure has been discussed in detail by Burrau.* In attempting to construct a model for this system we can suppose that the electron is bound by one nucleus to form a normal hydrogen atom, and the other nucleus is brought up slowly to a small distance from the first. For such systems it was discovered by Heisenberg and Dirac† that the perturbations of the electron by the second nucleus can lead to an oscillation of the electron between orbits around the two nuclei ; this oscillation introduces a new term into the expression which gives the total negative energy of the system, i.e. the work required to break up the system. This quantity

* *Det. Kgl. Danske Videnskabernes Selskab. Math-fys Meddelelser*, 1927, **7**, 14. A more accessible account of this work is given by Pauling, *Chem. Rev.*, 1928, **5**, 185.

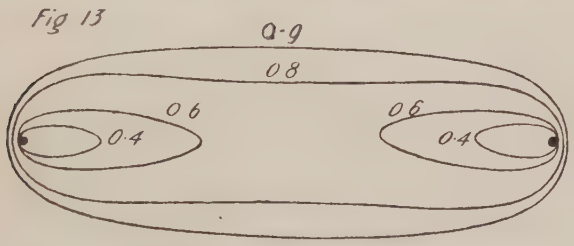
† Heisenberg, *Z. f. Physik*, 1926, **38**, 411 ; **39**, 499 ; 1927, **41**, 239 ; Dirac, *Proc. Roy. Soc.*, London, 1926 [A], **112**, 661.

is important, since it measures the stability of the system. The energy term due to oscillation may be positive or negative, depending upon the quantum numbers which define the levels of the oscillating electron about the two nuclei, and hence the *interchange* or *resonance energy* may either increase or decrease the stability. Burrau solved numerically the wave equations for this system, and calculated the value of the negative energy of the system for different distances r between the two nuclei; the results of these calculations are shown graphically in fig. 12. Here the ratio $W_{H_2^+}/W_H$ is plotted against r. In curve I the interchange energy is neglected and it will be seen



that this ratio is less than unity for all values of r. This signifies that the system is less stable than a separate hydrogen atom and a hydrogen nucleus for all values of r, so that a stable molecule cannot be formed. Curve II gives the ratio when the interchange has a sign which will increase the stability of the system; when r is greater than 1·1 Ångstrom units, $W_{H_2^+}$ becomes greater than W_H, and the stability of the system reaches a maximum with $r = 2{\cdot}0$; this corresponds to the formation of a stable molecule. In curve III the interchange energy has the opposite sign, $W_{H_2^+}$ is always less than W_H, and the impinging proton is repelled from the hydrogen atom. *It is therefore the interchange energy which makes possible the existence of a stable molecule and gives rise to a non-polar bond.*

From the wave equations the distribution of the electron in the region about the two nuclei can be calculated. That is, a set of contours can be drawn (fig. 13) which define the " electron density," and which can be defined statistically as indicating the probability that the electron will be found within a given region at a given moment. Thus, the outer curve marked 0·9 indicates that the relative chance that the electron is within this region is 0·9 and the chances that the electron at a given moment is with the contours marked 0·8 and 0·9 are as 8 : 9. When the interchange energy has the sign which gives a stable molecule, these contours are elongated so as to lie for the most part between the two nuclei ; that is, the electron tends to occupy the region between the nuclei and is " shared " by them. Furthermore, these curves are sections of figures of revolution about an axis through the



nuclei, and so represent a linkage due to sharing as a bond with a definite space direction. This is, of course, an essential property of a chemical non-polar bond.

The problem of the structure of the hydrogen molecule, H_2, was discussed independently by Heitler and London,* with results which are very similar to those found for the hydrogen molecule ion. Here two electrons oscillate between the two nuclei, giving in this case a duplet link. As before, it is the interchange energy which determines the formation of a stable molecule, and the space distribution of the electrons in the stable molecule again shows that they are shared, and that the bond so produced has a definite space direction. Furthermore, Heitler and London showed that in the case of helium the limits set by Pauli's principle to the quantum numbers of the electrons in an atom (cf. p. 70), make the interchange energy have a sign which always leads to repulsion between two

* *Z. f. Physik*, 1927, **44**, 455.

approaching helium atoms. Hence the wave-mechanics theory explains why two hydrogen atoms form a molecule and two helium atoms do not.

General Quantum Theory of Covalencies. (1) Normal Valencies

The extension of the quantum theory to more complex systems has been discussed by Heitler,* London,† and Pauling.‡ In particular London has developed a general theory of covalencies which, with some modifications, harmonises with the conclusions reached on chemical and physico-chemical evidence.

According to London the capacity to form a covalent linkage depends upon the resultant spin quantum number of the atomic state, and the sharing of electrons consists essentially of a neutralisation or coupling of the spins of electrons in two atoms. The valency of an atom is defined as one unit smaller than the multiplicity of the term corresponding to the atomic state, and is equal to the resultant spin quantum number measured in units of $h/4\pi$. It is, therefore, equal to $2S$ where S is Hund's spin quantum number for the atomic state (p. 71). To saturate a valency it is necessary that the foreign electron (coming from the second atom taking part in the bond) be antiparallel in its spin to the first. The saturation of a valency is therefore accompanied by a reduction of one unit in the resultant spin quantum number of the system; when all the covalencies are satisfied the resultant spin of the whole system becomes zero.

As an example we may take the valencies of the carbon atom. In the normal state the electrons will have the quantum numbers shown in scheme I below. It is very convenient to write the quantum numbers l, m_l, and m_s in this order for each electron, and so obtain a concise representation of the atomic state. The principal quantum number can be neglected and m_s is conveniently written in units of $h/4\pi$ to avoid repetition of the fraction $\frac{1}{2}$.

In I the electrons are grouped in pairs in which the spin quantum numbers balance. The value of m_l for the second pair may be either -1, 0, or $+1$. Any of these arrangements

* *Z. f. Physik*, 1927, **46**, 47; 1928, **47**, 835.
† *Ibid.*, 1928, **46**, 455.
‡ *Proc. Nat. Acad. Sci.*, 1928, **14**, 359.

	m_l	m_s
0	0	+
0	0	−
1	0	+
1	0	−

$2S = 0$

I

l	m_l	m_s
0	0	+
0	0	−
1	$\bar{1}$	+
1	0	+

$2S = 2$

II

l	m_l	m_s
0	0	+
1	$\bar{1}$	+
1	0	+
1	1	+

$2S = 4$

III

gives a resultant spin vector for the atom of 0, and according to London's theory this corresponds to a valency of 0. In state II, two of the electrons have different values of m_l, hence, without violating Pauli's exclusion principle (p. 70), they can have spins in the same direction. This gives a resultant spin vector of 2 units and corresponds to divalent carbon. In III all four electrons have different values of m_l, and can therefore have the same spins; the resultant spin vector is now 4 units corresponding to a valency of 4.

The saturation of these valencies by electrons from four hydrogen atoms to form the molecule of methane may be represented diagrammatically as shown in scheme IV. Here the four electrons with +spins from the carbon atom are shared by occupying vacant levels for electrons with +spins in the hydrogen atoms; the interchange is indicated by the symbol ←——→. Similarly the electrons from the hydrogen

										Ne	
C	0	0	+	←——→	0	0	+	} H	0	0	+
	0	0	−	←——→	0	0	−		0	0	−
	1	$\bar{1}$	+	←——→	0	0	+	} H	1	$\bar{1}$	+
	1	$\bar{1}$	−	←——→	0	0	−		1	$\bar{1}$	−
	1	0	+	←——→	0	0	+	} H	1	0	+
	1	0	−	←——→	0	0	−		1	0	−
	1	1	+	←——→	0	0	+	} H	1	1	+
	1	1	−	←——→	0	0	−		1	1	−

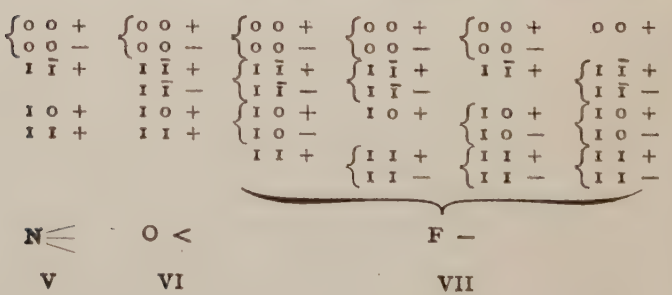
IV V

atoms occupy the vacant levels with −spins in the carbon atom. In methane the carbon atom has then eight electrons with the same disposition of quantum numbers as the eight electrons which form the stable octet in neon (V) and the other inert gases.

(This method of representing shared electrons is not given by

London, but appears to the writer to be a simple and convenient method of representing the consequences of London's theory. One point in connexion with such formulæ may be mentioned here. The quantum number m_l represents the projection of the magnetic moment of the electron in its orbit in a direction parallel to that of a weak external magnetic field, hence these numbers define the relative space directions of the orbits which the electrons may be supposed to occupy in the two atoms. Thus, when $l = 1$, $m_l = 1$ signifies an orbit with its plane at right angles to the field and its magnetic effect parallel to the field. When $m_l = -1$, the orbit is in the same plane, but the electron is moving in the opposite direction giving a magnetic field which opposes the external field. When $m_l = 0$ the plane of the orbit is parallel and the magnetic field is normal to the external field. If these numbers are still valid for shared electrons (which is somewhat doubtful) then the first and third electrons in IV, which have the same value of m_l for the levels they occupy in both atoms, will therefore have the loops of their orbits around these atoms in the same plane. The second and third electrons are shared between levels for which m_l differs by one unit, which would appear to mean that the part of the orbit around the carbon atom is in a plane at right angles to the plane of the orbit around the hydrogen atom. This twisting of the orbits of certain shared electrons appears to be inevitable if the m_l numbers have the same significance for shared electrons as they have in Hund's scheme for isolated atoms.)

The normal valencies of the elements are readily accounted for by London's theory. Since the outermost electrons are occupying levels for which $l = 0$, or 1, then atoms with 1, 2, 3, or 4 valency electrons can have all the electrons with spins in



the same direction without violating Pauli's rule ; the resultant spin vectors, and hence the valencies, are therefore 1, 2, 3, and 4. When more than four electrons are present the operation of Pauli's rule limits the allocation of spin quantum numbers to the electrons, and gives a maximum resultant spin vector for the atom of 3, 2, and 1 with atoms containing 5, 6, and 7 electrons. Formulæ V, VI, and VII show the arrangement of quantum numbers for, say, trivalent nitrogen, divalent oxygen, and monovalent fluorine. The pairs of electrons with balanced spins are bracketed. It is evident that the choice of the electrons which are left unpaired is arbitrary, and four alternative arrangements for monovalent fluorine are shown to illustrate this point.

Higher Valencies. The Octet Rule

The higher valencies of nitrogen in the ammonium salts, etc., are explained by London in the following manner. In the ammonium salts the nitrogen atom loses an electron which is taken up by an electro-negative atom, e.g. chlorine, to form an anion. The remaining four electrons can then be allocated quantum numbers in exactly the same manner as the four electrons in the carbon atom, so that the structure of the NH_4 ion can be represented by the same scheme of quantum numbers as that used for methane (IV). It is obvious that a similar explanation can be given for the semipolar double bonds in nitro-compounds, phosphates, sulphates, perchlorates, etc.

The higher valencies of elements in the second and third periods of Mendeléef's table are explained in a different manner. After neon the valency electrons are bound in levels with a principal quantum number of 3 or more, so that l is no longer restricted to the values 0 and 1, but may have the value 2, when $n = 3$, and still higher values when n is greater. This permits of the splitting of more balanced pairs of electrons in the atom and the attainment of a higher resultant spin without violating Pauli's principle. For pentavalent phosphorus, hexavalent sulphur, and heptavalent chlorine, London suggests the distribution of quantum numbers shown in formulæ VIII, IX, and X.

Such an arrangement will permit linkages composed of shared pairs to be formed with 5, 6, and 7 other atoms, thus giving shells of 10, 12, and 14 electrons around the central atom. It

P^{V}			S^{VI}			Cl^{VII}		
0	0	+	0	0	+	0	0	+
1	$\bar{1}$	+	1	$\bar{1}$	+	1	$\bar{1}$	+
1	0	+	1	0	+	1	0	+
1	1	+	1	1	+	1	1	+
2	$\bar{2}$	+	2	$\bar{2}$	+	2	$\bar{2}$	+
			1	$\bar{1}$	+	2	$\bar{1}$	+
						2	0	+
VIII			IX			X		

is this part of London's theory which is most open to criticism,* and which in the writer's opinion requires modification.

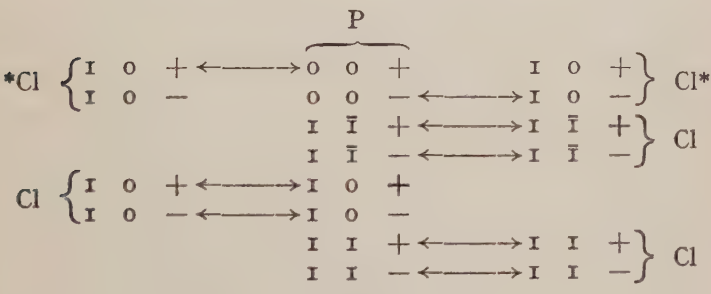
In the first place it seems improbable that orbits with serial quantums greater than $l = 1$ ($k = 2$) will be occupied in these atoms. In the isolated atoms these levels only begin to be filled after a level of higher principal quantum number is partially occupied, as in scandium and the elements in the first transition series. Furthermore, London's hypothesis gives no reason for the limitation of the maximum covalency of an atom to 8. Thus, for example, in palladium, if the l values can be chosen at will a maximum covalency of 10 appears possible. In the normal state of this atom the 10 electrons fill the 4_3 level, and have the paired spins shown in XI. By distributing these electrons between the 4_3 and 4_4 levels a maximum spin vector for the atom of 10 units can be attained as in XII, and ten covalent links should be possible. The maximum covalency ever found in a stable chemical compound is, however, 8, as in OsF_8.

2	$\bar{2}$	+	2	$\bar{2}$	+
2	$\bar{2}$	−	2	$\bar{1}$	+
2	$\bar{1}$	+	2	0	+
2	$\bar{1}$	−	2	1	+
2	0	+	2	2	+
2	0	−	3	$\bar{3}$	+
2	1	+	3	$\bar{2}$	+
2	1	−	3	$\bar{1}$	+
2	2	+	3	0	+
2	2	−	3	1	+
XI			XII		

* Cf. Rodebush, *Nature*, 1928, **122**, 56.

Another difficulty is met with in co-ordination compounds, e.g. aluminium acetylacetonate. From the stereochemical evidence the molecule of this substance undoubtedly possesses six covalent linkages on the aluminium atom, yet the latter has only three valency electrons which can give a maximum spin of 3 units only. The only way in which a spin of 6 units could be attained is the transfer of three electrons from oxygen atoms to the aluminium, and this is highly improbable on electrochemical grounds (cf. pp. 134, 148).

The higher valencies can all, however, be accounted for by using singlet linkages to construct the formulæ. The chemical and physicochemical evidence for such linkages has been discussed in chapters VI and VII, whilst Burrau's work shows that the singlet in H_2^+ has similar properties to the duplet in the hydrogen molecule. It is, therefore, justifiable to use such a linkage in constructing a quantum theory of valency. All the singlet formulæ given in earlier chapters are readily described in terms of quantum numbers; a simple example is furnished by phosphorus pentachloride, for which the distribution of quantum numbers is given in formula XIII. For



XIII

clearness only two of the electrons in each chlorine atom are shown; the remainder form pairs with balanced spins. The chlorine atoms marked with an asterisk are held by singlet linkages; the other three are bound as usual by duplets. Similar formulæ can readily be written for SF_6, OsF_8, and the co-ordinated derivatives of acetylacetone, etc. This method of accounting for higher valencies has two advantages over that suggested by London. It involves no azimuthal quantum numbers which are not already allocated to electrons in the

isolated atom, and in most stable molecules it gives an outer shell of eight electrons with the same distribution of quantum numbers as that of the octet in the inert gases.

Here again this outer shell of eight electrons appears to play an important part in the structure of molecules. The number of electrons in the shell is of course fixed by Pauli's rule, if only the levels for which $l = 0$ and $l = 1$ are occupied. No physical explanation has yet been given for this limitation of the l values, nor for the remarkable stability which the possession of this shell confers on atoms and molecules. Possibly the development of the wave-mechanics will throw some light on this important problem which is so intimately concerned with the electronic theory of valency.

CHAPTER XI

EXPERIMENTAL METHODS

Density Determinations

THE measurement of the parachor involves determinations of the surface tension and density of a substance in the liquid state. In many cases the substances to be studied are solids at ordinary temperatures, and may have high melting points; the methods chosen to measure these constants should, therefore, be readily manipulated at moderately high temperatures and give results of sufficient accuracy. The surface tension methods described in the following section can be used with little modification up to 300°; the density determinations give more trouble, and the usual type of pyknometer is of little use for substances melting above 50°.

Fig. 14 shows a type of pyknometer which has been found suitable for use with high-melting substances, and readily gives a series of densities over a range of temperatures. It consists of a U-tube, one limb of which has an internal diameter of about 10 mm., whilst the other is made of capillary tube of about 2 mm. internal diameter. A bulb of about 1·5–2·0 c.c. capacity is blown on the lower end of the capillary limb, and the capillary tube extends beyond the bulb to form a junction with the wider tube. A reference mark is etched on this tube at A, and a scale of equal divisions on the capillary above the bulb; this scale is numbered upwards from a zero near the bulb.

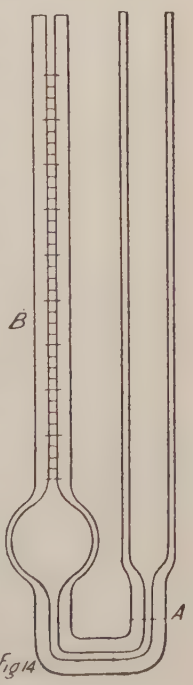


Fig 14

The apparatus is calibrated by determining the weight of water which fills it from A

to a series of points on the scale B. For this purpose the weighed pyknometer is supported vertically in a bath of water at a known temperature, and a suitable quantity of boiled distilled water introduced into the wide limb. The open end of the capillary limb is then connected to a small mercury aspirator with a capillary jet. By applying slight suction the water is drawn into the bulb so that one meniscus is at A and the other at some point on the scale. The wide tube is then wiped out with a strip of folded filter paper and, after standing 15 minutes to acquire the bath temperature, the scale reading is noted. The pyknometer is then withdrawn from the bath, dried externally, and weighed. From a series of observations of this kind the volume of the bulb and of the scale divisions is tabulated. The coefficient of expansion of the glass can be determined by making similar observations with mercury from room temperature to 200°; in this experiment the apparatus and the mercury must be very thoroughly dried, for small traces of moisture adhering to the glass produce bubbles at the mercury glass interface above 100° C., and cause a large error in the observed volume. Since the correction for expansion is small up to 300°, it is usually unnecessary to make this rather troublesome experiment, and instead one may calculate the volume of the pyknometer at higher temperatures using a coefficient of expansion of $2{\cdot}5 \times 10^{-5}$, which is valid for most soft soda glasses.

To measure the density of a substance which is solid at room temperature the weighed pyknometer is supported in a suitable bath heated to a few degrees above the melting point. (Benzyl benzoate is a useful bath liquid up to 250°, and has the advantage over glycerine that it is mobile at room temperatures and has a smaller specific heat so that it can be rapidly raised to the desired temperature.) The roughly powdered solid is gradually introduced into the wide limb of the pyknometer, and when melted is drawn into the bulb. Further small quantities of solid are added cautiously until the molten substance fills the apparatus from A to some point on the lower part of the scale. The wide tube is then wiped out as before and, after thermal equilibrium is attained, the volume of the liquid is read off. The temperature of the bath is then raised 10°, and after 10–15 minutes the volume reading should again be steady at its new value and is noted. In this way a series of observations of the volume at different temperatures is

obtained, care being taken that at no time is the level of the liquid in the capillary brought above the bath level. With this apparatus the liquid can readily be manipulated below the bath level and so no difficulties are encountered due to the solidification of the substance in the capillary. A pyknometer of the dimensions given will usually give densities over a range of 50° at one filling. When all the desired volume observations have been made the liquid is blown back into the wide limb and allowed to solidify there when the pyknometer is removed from the bath. (This facilitates the cleaning of the instrument.) The pyknometer is then cleaned externally and weighed to determine the amount of substance used.

The chief source of inaccuracy to be guarded against is the drainage error in the wide tube. This is minimised by wiping out the tube with filter paper after a suitable amount of substance has been melted and drawn into the bulb. It is advisable, however, to take volume readings at 5-minute intervals with a steady bath temperature. These usually become constant after 10 minutes, but with viscous liquids 30 minutes may be necessary.

The formula for the parachor involves the vapour density as well as the density of the liquid, but unless the temperature of measurement approaches the boiling point this is very small and can be neglected. If vapour pressure observations are available the vapour density can readily be calculated assuming that the gas laws hold for the vapour ; below the boiling point this assumption is sufficiently accurate. Another method of calculating the vapour density d can also be used.* If T_b is the boiling point at 760 mm. expressed in degrees absolute, then from the gas laws the vapour density at the boiling point is $d_b = 0{\cdot}0122\ M/T_b$, where M is the molecular weight. The value of d at lower temperatures can then be calculated by the empirical relation

$$log._{10} d/d_b = 5(T/T_b - 1)$$

This expression gives the vapour density to within $\pm$ 0·0002 gm./c.c., and is amply accurate for parachor calculations.

Surface Tension Measurements. (a) Capillary Rise

The measurement of surface tension from the rise in capillary tubes is one of the oldest methods used to determine this

* Sugden, *J.C.S.*, 1925, **127**, 1540.

property of a liquid. Many variations are possible in the form of the apparatus used for this purpose; it will suffice to describe one form which has proved useful when the properties of the liquid necessitate the employment of a sealed vessel. This is essential when very hygroscopic substances have to be examined, or with substances which can only be liquefied under pressure, e.g. PCl_5.

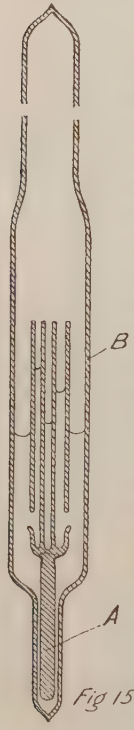


Fig 15

For accurate work it is desirable to measure the difference in the level to which the liquid rises in two tubes of circular cross-section and different radii; the form of the meniscus is then given by the equation developed in the mathematical theory on page 215, and the method there given for calculating the surface tension can then be applied. A convenient method of supporting the tubes is shown in fig. 15. Here the glass rod A serves as a support to hold the tubes upright in the bulb B. The outer tube above the bulb is wide enough to allow the capillaries and their support to be withdrawn for cleaning and re-measurement of their radii if this becomes necessary.

To construct the instrument thin-walled capillary tubing is cut into about 10 cm. lengths and examined by means of a reading microscope. All tubes showing a deviation from a circular cross-section of more than 2%, or a difference in diameter at opposite ends of the tube of more than 1%, are rejected. The tubes are also examined throughout their length to see that the walls are parallel and free from irregularities. Two suitable tubes are then sealed together and sealed on to the glass rod which is chosen to fit smoothly into the socket at the lower end of B. Small holes are blown in the lower ends of the tubes and the upper ends cut off level leaving a length of about 5 cm. The internal diameters of the open ends of the tubes are then measured with a reading microscope; four diameters at angles of 45° should be measured and the mean value taken.

This apparatus was designed for use with a reading microscope using an objective of 3″ focal length, and a bifilar micrometer eyepiece. This contains a fixed thread and a

parallel moving thread controlled by a micrometer screw and drum. With both menisci in the field of view the fixed thread is set tangentially to the base of one meniscus, and the moving thread to the base of the other ; the difference in level is then obtained from the reading of the drum. This method is rapid and accurate, but it is essential that both menisci should be visible simultaneously in the field of view of the microscope. For this reason the tubes have to be chosen with radii which will not give too large a difference in level (< 8 mm.) ; on the other hand the wider tube must give a sufficient capillary rise to lift the meniscus clear of the level of the liquid in the outer vessel. As a rough guide in selecting suitable tubes the following figures are useful.

Specific cohesion of liquid.	r_1	r_2
10–15 mm.^{2}	0·08 cm.	0·15 cm.
5–10 mm.^{2}	0·06 cm.	0·13 cm.
2– 5 mm.^{2}	0·04 cm.	0·07 cm.

The first pair of tubes is suitable for liquids like water with a high surface tension and a moderate density ; the second pair gives a convenient apparatus for dealing with most organic liquids. The third pair is useful for substances with low surface tensions and high densities, e.g. ethylene dibromide and aluminium bromide.

In making a measurement the apparatus is first cleaned thoroughly by filling with a 10% solution of chromic acid in 40% nitric acid and heating in a water-bath for an hour. The instrument is then well washed with distilled water, heated in the steam oven, and dried by the repeated passage of a current of filtered air, blown in through a tube reaching nearly to the bottom of the bulb. A suitable quantity of the substance to be examined is then introduced and the upper end of the instrument is sealed off. The apparatus is supported in a suitable bath with the capillary tubes vertical ; this adjustment is conveniently made by focussing the reading microscope alternately on the tubes and on a small plumb-line suspended close to the tube. The difference in height between the two menisci is then determined by means of the bifilar micrometer as described above. The chief difficulty met with at higher temperatures is the error due to optical irregularities in the wall of the beaker holding the bath, and similar errors due to

convection currents in the bath liquid. These are avoided as far as possible by making several observations through different parts of the wall of the beaker and by stirring the bath vigorously immediately before each observation.

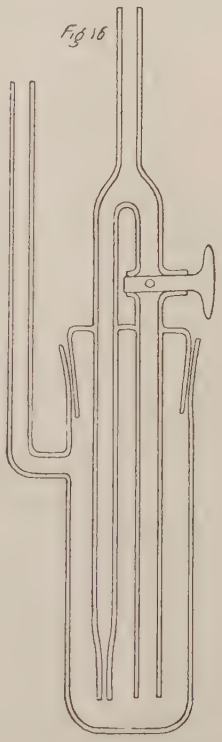
To ensure thorough wetting of the tube above the meniscus the apparatus is rocked and shaken gently before each reading is taken. With the comparatively wide tubes used the level of the liquid rapidly attains a constant level in the tubes except with liquids of very high viscosity. With such substances observations must be taken at regular intervals until a constant reading is found.

The calculation of the surface tension from the observed data is discussed on page 219. This method is much more tedious than the method of bubble pressure described below, and suffers from two serious disadvantages. The result is affected by the contact angle of the liquid with glass and is equal to the surface tension only when the contact angle is zero. Also it is necessary in this method to observe the capillary rise through the bath liquid, and at high temperatures this introduces serious difficulties and possible errors. For these reasons the capillary rise method has been employed by the author only in those cases in which the properties of the substance necessitated the use of a sealed vessel.

Surface Tension Measurements. (b) Maximum Bubble Pressure

The apparatus used for this method is shown in fig. 17, and consists essentially of three parts, the bubbler, the gauge, and the aspirator. The bubbler is shown on a larger scale in fig. 16 ; the outer vessel is about 2 cm. in diameter and 8 cm. long, with a side tube about 8 cm. long extending to a convenient distance above the bath level. This vessel is closed by a ground-in stopper through which the experimental tubes are sealed. A well-fitting tap is inserted in the wider tube and above this tap the tubes are joined as shown in the figure. The wider tube is conveniently chosen to have an internal radius of about 0·15 cm. ; the capillary is drawn out and cut off level with the wider tube and should have a radius of between 0·005 and 0·010 cm. After a little practice the size of capillary required is readily estimated by the eye when drawing out the tube. The best test is to set up the apparatus as described below and take a rough reading with a little benzene

in the bubbler. If the capillary is of a suitable size a reading of between 4 and 8 cm. on the gauge will be obtained. The bubbler is readily cleaned by immersing the whole apparatus in hot nitric and chromic acids, and subsequently washing with distilled water. For work with organic liquids the apparatus may then be rinsed with absolute alcohol, followed by benzene, and dried in the steam-oven. For aqueous solutions or water, the apparatus is best washed free from chromic acid by tap water (which is usually not so likely to introduce grease as distilled water), and is then rinsed out several times with the solution to be examined. Since grease cannot be used on the ground joint or tap it is necessary that these should fit well.



The gauge consists of a water-jacketed U-tube filled with tinted absolute alcohol, and supported in front of an opal glass millimetre scale; the temperature of the gauge is given by a thermometer immersed in the water jacket. From a few observations of the density of the specimen of alcohol used between 0° and 30°, a table is readily constructed by which gauge readings at any temperature within these limits can be converted directly into dynes/cm.^{2}.

The mercury aspirator is readily constructed from a small dropping funnel, fitting into a wide-mouthed bottle as shown in the figure. The delivery tube of the dropping funnel is drawn out into a capillary jet of such a size that a ready control of the formation of bubbles can be obtained by partially closing the tap. For smooth working it is essential to maintain an unbroken column of mercury between the tap and the capillary jet.

The outer vessel of the bubbler is supported in a suitable bath with stirrer and thermometer, and is connected to the gauge and aspirator by light rubber tubing. A quantity of

liquid is used which will cover the ends of the tubes to a depth of 2–3 mm. when the stopper is inserted. The tap leading to the wider tube is closed and the aspirator started. Bubbles soon commence to issue from the capillary tube and the rate of flow of mercury in the aspirator is then adjusted until single bubbles are formed at the rate of about one per second. A slight oscillation of the gauge will be noted as each bubble is detached, and the maximum pressure recorded by the gauge

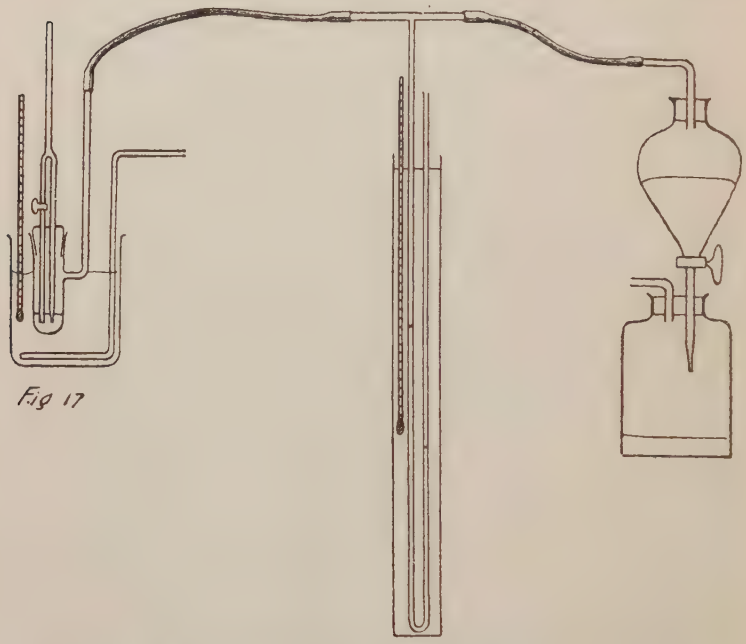


Fig 17

is noted. If the apparatus is not clean the bubbles are not formed smoothly, but come in groups of three or more and the gauge oscillates over a range of several millimetres. If this occurs the readings should be rejected and the apparatus taken down and cleaned. When a satisfactory reading has been obtained for the capillary, the tap is opened and bubbles form from the wider tube. In this case the development of a maximum pressure as the bubble grows is readily observed, and this maximum is recorded. The difference between the maxima found for the two tubes is the quantity H from which the surface tension is calculated.

The internal radius of the wider tube is readily determined by means of a reading microscope. Direct measurement of the radius of the capillary in the same way is more difficult and tedious, and the apparatus is conveniently calibrated by using benzene as a standard liquid. The surface tension of benzene at every degree from 10° to 30° is given below; if the calibration observation is made at room temperature, the corresponding surface tension of benzene is readily obtained by interpolation from these figures.

$t.$	γ dyn./cm.	$t.$	γ dyn./cm.	$t.$	γ dyn./cm.	$t.$	γ dyn./cm.
10°	30·19	15°	29·53	20°	28·88	25°	28·23
11°	30·05	16°	29·40	21°	28·75	26°	28·10
12°	29·92	17°	29·27	22°	28·62	27°	27·97
13°	29·79	18°	29·14	23°	28·49	28°	27·84
14°	29·66	19°	29·01	24°	28·36	29°	27·71
						30°	27·58

Traces of common impurities, e.g. thiophene and cyclohexane, have no appreciable effect upon the surface tension of benzene, so that a specimen for use as a standard liquid is readily prepared as follows: "Crystallisable" benzene is frozen out once rejecting about one-third as a more fusible fraction. The remainder is then distilled using an efficient column, and the fraction boiling at 80°–80·5° collected and stored over sodium if desired. It is found, however, that dry benzene and benzene saturated with water give the same surface tension by the method of maximum bubble pressure.

The theory of the method of maximum bubble pressure is discussed on page 217, and a table is there given by means of which the surface tension can be calculated from observations on tubes of any size. For tubes with the radii defined above the simple formula

$$\gamma = AP\phi \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

can be used. Here P is the difference between the pressures required to liberate bubbles from the two tubes and A is a constant for the apparatus which depends chiefly upon the radius of the capillary. ϕ is a correction factor given by

$$\phi = 1 + 0{\cdot}69 r_2 gD/P \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where r_2 is the radius of the wide tube in cm., $g = 981$ cm./sec.^{2}, D is the density of the liquid, and P the pressure difference

as before. As an example of the method of calculation, a few figures for benzene will be given in detail.

The bubbler used had $r_2 = 0{\cdot}159$ cm. At 20°, with benzene, $H = 10{\cdot}90$ cm. The gauge temperature was 14°; at this temperature the factor for converting gauge readings into dyn./cm.^{2} is 780·5, hence $P = 10{\cdot}90 \times 780{\cdot}5 = 8508$ dyn./cm.^{2}. At 20° $D = 0{\cdot}877$, and from equation (2) this gives $\phi = 1{\cdot}0111$. For benzene at 20° γ is 28·88 dyn./cm., hence from equation (1)

$$A = \gamma/P\phi = 0{\cdot}003358$$

This constant can now be used to calculate surface tensions from observations on any liquid with this apparatus. As an example some observations on benzene at other temperatures may be quoted.

t.	*H* cm.	*Gauge temp.*	*Gauge factor.*	*P.* dyn./cm.^{2}	*D.* gm./c.c.	ϕ	γ dyn./cm.
13·5°	11·20	12·5°	781·7	8757	0·885	1·011	29·72
34·5°	10·18	14°	780·5	7943	0·862	1·012	26·98
72°	8·34	14°	780·5	6510	0·819	1·0135	22·15

P is obtained by multiplying H by the gauge factor; ϕ is then calculated by equation (2), and the surface tension by equation (1), using the value of A given above.

Mathematical Theory of Surface Tension Measurements

(a) General Equation to a Liquid Surface

In most of the methods of measuring surface tension the boundary of the liquid is a surface of revolution about a vertical axis; the shape of this surface is determined by the forces at each point on it due to surface tension and to gravity.

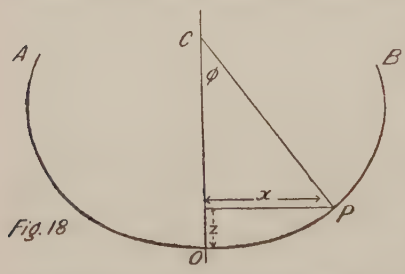


Fig. 18

Let AOB (fig. 18) be the section of such a surface by a plane passing through the axis of revolution OC. Let any point P on the surface be defined by co-ordinates x and z referred to the tangent and normal at O as axes. Let

the angle between the normal at P and the axis OC be ϕ.

From the general equation of Laplace (p. 7) the difference in pressure between the inside and outside of such a surface is equal to

$$\gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$

where R_1 and R_2 are the principal radii of curvature of the surface at P. At O these radii become equal; if the radius of curvature at this point is b, then the excess of pressure inside the surface at O is $2\gamma/b$. At P the pressure difference is greater by an amount $gz(D - d)$, where g is the acceleration due to gravity, D the density of the liquid below the surface, and d the density of the gas + vapour above it. Hence

$$\gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = gz(D - d) + \frac{2\gamma}{b} \quad \ldots\ldots\ldots\ldots (1)$$

Since we are dealing with a surface of revolution one of the radii of curvature is $PC = x/\sin\phi$. The second radius is the radius of curvature of AOB at P; let its value be ρ. Then (1) becomes

$$\gamma\left(\frac{\sin\phi}{x} + \frac{1}{\rho}\right) = gz(D - d) + \frac{2\gamma}{b}$$

Dividing out by γ/b

$$\frac{\sin\phi}{x/b} + \frac{1}{\rho/b} = \frac{g(D - d)b^2}{\gamma} \cdot \frac{z}{b} + 2$$

$$= \beta \cdot \frac{z}{b} + 2 \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where $\beta = g(D - d)b^2/\gamma$.

In equation (2), ρ and $\sin\phi$ can be expressed in terms of the first and second differential coefficients of z with respect to x, thus giving the differential equation

$$\frac{d^2z'}{dx^2} + \left\{1 + \left(\frac{dz}{dx}\right)^2\right\} \cdot \frac{dz}{xdx} = (2 + \beta z)\left\{1 + \left(\frac{dz}{dx}\right)^2\right\}^{3/2} \quad \ldots (3)$$

This equation represents a family of curves each member of which corresponds to a definite numerical value of β. When β is small the curve AOB is approximately a circle, and the surface is approximately spherical. For finite surfaces the curvature changes appreciably on passing from O to B, and must be determined from equation (2) or (3).

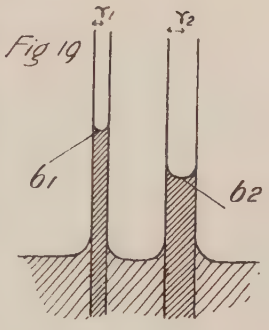
An explicit integration of equation (3) is impossible ; that is, we cannot find any expression made up of simple well-known functions which will give the general relation between x and z for these curves. By suitable mathematical methods we can, however, obtain numerical solutions of particular cases of a differential equation of this kind to any desired degree of accuracy. For equation (3) a large number of such solutions have been worked out by Bashforth and Adams.* There are two important cases to be considered which require different treatment ; these are distinguished by the sign of β. The first case in which β is positive corresponds to a liquid in a capillary tube, a bubble emerging from the lower end of a tube dipping vertically into the liquid, or to drops of mercury resting on a horizontal plate. The second case in which β is negative corresponds to a pendent drop, or to a bubble emerging upwards from a tube immersed in the liquid. The second case is much more difficult to deal with mathematically than the first, and an accurate solution is not possible since, at a certain stage in the development of the drop or bubble, a neck forms and rapid changes in shape follow. The system can therefore no longer be regarded as one which is in equilibrium ; equation (3) no longer holds and a dynamical treatment of the problem is required (cf. p. 12). For the first case in which β is positive these difficulties are not met with, and Bashforth and Adams give a complete series of solutions of equation (3) for values of β ranging from $\beta = 0{\cdot}1$ to $\beta = 50$. These have recently been extended to higher values of β by Bosanquet.†

These solutions are set out in the form of tables in which under each value of β the ratios x/b and z/b are tabulated to five significant figures for points on the surface corresponding to values of ϕ from 0° to 180° at 5° intervals. For any known value of β it is therefore possible to draw the outline AOB by using the numbers in these tables. Since, however, these tables give a complete solution of equation (3), they can also be used to solve any problems in which surfaces are concerned to which this equation applies. In this way an accurate theory for the methods commonly used in the measurement of surface tension can be obtained.

* *Capillary Action*, Camb. Univ. Press, 1883.
† *Phil. Mag.* [7], **6**, 296.

(b) Theory of the Method of Capillary Rise

Consider two tubes of radii r_1 and r_2, dipping vertically into a liquid (fig. 19). Let the difference in height between the lowest points on the menisci be H, and let the radii of curvature at these points be b_1 and b_2. Then from Laplace's equation the difference in pressure between these two points in the liquid is $2(1/b_1 - 1/b_2)$. This must, however, be equal to the hydrostatic pressure $Hg(D - d)$. Hence



$$a^2 = \frac{2\gamma}{g(D-d)} = \frac{H}{\frac{1}{b_1} - \frac{1}{b_2}} \quad \ldots\ldots\ldots\ldots(4)$$

This equation is strictly true whatever the radius of the tube, but it gives a^2 (or γ) in terms of the unknown quantities b_1 and b_2. If the liquid wets glass and the angle of contact is 90°, then the upper edge of the meniscus where it touches the tube corresponds to $\phi = 90°$ in Bashforth and Adams' tables. We can, therefore, tabulate values of r/b (the x/b of B. and A.) corresponding to different values of β and $\phi = 90°$. Further, since

$$\beta = \frac{g(D-d)b^2}{\gamma} = \frac{2b^2}{a^2}$$

then

$$\frac{r}{a} = \frac{r}{b}\sqrt{\beta/2}$$

From the values obtained from Bashforth and Adams' tables we can, by interpolation, construct a new table giving r/b as a function of r/a. This table is given on page 216 and covers all possible values of r/b. The latter part of the table is based upon certain approximate formulæ valid for large values of r/a.*

This table can be used to calculate accurate surface tensions when the values of r_1, r_2, and H are known. When r/a is small r/b is nearly unity and does not vary rapidly with r/a. Hence by assuming that $r = b$ we can get a rough value for a^2 which can then be used to calculate r/a. From the table

* For a discussion of this range see Sugden, *J.C.S.*, 1921, **119**, 1483; *J. Amer. Chem. Soc.*, 1925, **47**, 60.

TABLE 79

Values of r/b for Values of r/a from 0·00 to 2·29

	0·00	0·01	0·02	0·03	0·04	0·05	0·06	0·07	0·08	0·09
0·00	1·0000	9999	9998	9997	9995	9992	9988	9983	9979	9974
0·10	0·9968	9960	9952	9944	9935	9925	9915	9904	9893	9881
0·20	9869	9856	9842	9827	9812	9796	9780	9763	9746	9728
0·30	9710	9691	9672	9652	9631	9610	9589	9567	9545	9522
0·40	9498	9474	9449	9424	9398	9372	9346	9320	9293	9265
0·50	9236	9208	9179	9150	9120	9090	9060	9030	8999	8968
0·60	8936	8905	8873	8840	8807	8774	8741	8708	8674	8640
0·70	8606	8571	8536	8501	8466	8430	8394	8358	8322	8286
0·80	8249	8212	8175	8138	8101	8064	8026	7988	7950	7913
0·90	7875	7837	7798	7759	7721	7683	7644	7606	7568	7529
1·00	7490	7451	7412	7373	7334	7295	7255	7216	7177	7137
1·10	7098	7059	7020	6980	6941	6901	6862	6823	6783	6744
1·20	6704	6665	6625	6586	6547	6508	6469	6431	6393	6354
1·30	6315	6276	6237	6198	6160	6122	6083	6045	6006	5968
1·40	5929	5890	5851	5812	5774	5736	5697	5659	5621	5583
1·50	5545	5508	5471	5435	5398	5362	5326	5289	5252	5216
1·60	5179	5142	5106	5070	5034	4998	4963	4927	4892	4857
1·70	4822	4787	4753	4719	4686	4652	4618	4584	4549	4514
1·80	4480	4446	4413	4380	4347	4315	4283	4250	4217	4184
1·90	4152	4120	4089	4058	4027	3996	3965	3934	3903	3873
2·00	3843	3813	3783	3753	3723	3683	3663	3633	3603	3574
2·10	3546	3517	3489	3461	3432	3403	3375	3348	3321	3294
2·20	3267	3240	3213	3186	3160	3134	3108	3082	3056	3030

Values of r/b for Larger Values of r/a

	0·0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9
2·0	0·384	355	327	301	276	252	229	206	185	166
3·0	149	133	119	107	097	088	081	074	067	061
4·0	056	051	047	043	039	035	031	028	025	022
5·0	020	018	017	015	014	012	010	009	008	007
6·0	006	006	005	004	004	003	003	003	002	002

the corresponding value of r/b can then be found, and hence b, from which a more accurate value of a^2 can be calculated. This will not be strictly accurate, since an incorrect value of a^2 was used to calculate r/a; by repeating the calculation, using the more accurate value of a^2, a closer approximation is obtained. Usually a few repetitions give a constant value of a^2 which can then be used to calculate the surface tension.

Thus, in an experiment with benzene at 20°, it was found that $H = 0{\cdot}7294$ cm. with tubes for which $r_1 = 0{\cdot}05495$ cm. and $r_2 = 0{\cdot}1310$ cm. From equation (4), assuming $r_1 = b_1$ and $r_2 = b_2$,

$$a^2 = \frac{H}{1/r_1 - 1/r_2} = 6{\cdot}905 \text{ mm.}^2$$

This approximate value of a^2 is now used to calculate r/a, giving

$$r_1/a = 0{\cdot}2092 \qquad r_2/a = 0{\cdot}4987$$

hence from table

$$r_1/b_1 = 0{\cdot}9885 \qquad r_2/b_2 = 0{\cdot}9239$$

whence

$$1/b_1 = 17{\cdot}93 \qquad 1/b_2 = 7{\cdot}05$$

so that

$$a^2 = 0{\cdot}7294/10{\cdot}88 = 6{\cdot}701 \text{ mm.}^2$$

If the calculation is now repeated, using this more accurate value of a^2, it is found

$$a^2 = 6{\cdot}696 \text{ mm.}^2$$

and further repetitions of this method of successive approximations gives no change in the value of a^2. At 20° $D = 0{\cdot}8785$, $d = 0{\cdot}0014$, $g = 981$, whence $\gamma = \frac{1}{2}a^2g(D - d) = 28{\cdot}81$ dyn./cm.

It is, of course, unnecessary to repeat this type of calculation for every observation. For a particular apparatus in which r_1 and r_2 are fixed, a few values of a^2 can be calculated for corresponding values of H, and the values for intermediate H's are then readily obtained by interpolation.

(c) Theory of the Method of Maximum Bubble Pressure

The calculation of the corrections for the method of maximum bubble pressure from Bashforth and Adams' tables is a little more complex, but can be dealt with in the following manner.*

In fig. 20 AOB represents the outline of a bubble emerging from the end of a vertical tube immersed to a depth t below the surface of a liquid. As the pressure inside the tube is increased, the size and the shape of the bubble change and the angle ϕ between the axis of the tube OC and the normal to the surface of the bubble at B increases. If b is the radius of curvature of the bubble at O, then the pressure in such a bubble is, in C.G.S. units, $p = 2\gamma/b +$

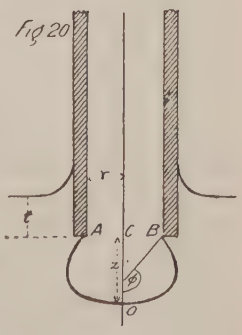


Fig. 20

* Sugden, *J.C.S.*, 1922, **121**, 859.

$zg(D - d)$ greater than the pressure at a point in the liquid t cm. below the surface. Here γ is the surface tension in dynes/cm., $z = OC$, g the acceleration due to gravity, D the density of the liquid, and d the density of the gas and vapour inside the bubble. This pressure would be exerted by a column of the liquid of height $h = P/g(D - d)$.
Hence

$$h = \frac{a^2}{b} + z \text{ and } \frac{hr}{a^2} = \frac{r}{b} + \frac{r}{a} \cdot \frac{z}{b} \cdot \frac{b}{a} \quad \ldots\ldots\ldots\ldots (5)$$

Now the form of the bubble is determined by the value of a quantity β, where

$$\beta = \frac{2b^2}{a^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

Putting this in (5), we have

$$(7)\ \frac{r}{X} = \frac{r}{b} + \frac{r}{a} \cdot \frac{z}{b}\sqrt{\beta/2}, \text{ where } X = \frac{a^2}{h} \quad \ldots\ldots\ldots (8)$$

For any given value of r/a there will be a number of values of r/X which correspond to a series of values of β, that is, to a series of values of ϕ. These can be calculated from (7) in conjunction with Bashforth and Adams' tables referred to above, as follows.

First, each value of r/b is calculated by the relation

$$\frac{r}{b} = \frac{r}{a} \cdot \frac{a}{b} = \frac{r}{a}\sqrt{2/\beta} \quad \ldots\ldots\ldots\ldots\ldots\ldots (9)$$

The angle ϕ corresponding with this value of r/b (the x/b of Bashforth and Adams' tables) and the quantity z/b for this angle are then obtained under the appropriate β from Bashforth and Adams' tables and inserted in (7) to calculate r/X. The following example will make this clear.

$r/a = 1{\cdot}0$

β	r/b.	z/b.	r/X.	ϕ.
6·0	0·5772	0·6756	1·7479	147·1°
6·5	0·5546	0·6640	1·7519	152·6
7·0	0·5346	0·6514	1·7536	157·5
7·5	0·5165	0·6384	1·7528	162·1
8·0	0·5000	0·6254	1·7508	166·5

It will be seen that as ϕ increases, r/X, which is proportional to the pressure in the bubble, passes through a maximum value which can readily be determined. For this value of r/a, which

corresponds with a tube 7 mm. in diameter immersed in water, the maximum is reached when ϕ is about 160°. It is only for infinitely small tubes that the maximum pressure corresponds with $\phi = 90°$.*

A series of minimum values of X/r can be calculated in this way for a range of values of r/a and from them, by careful interpolation, table 80 has been constructed. For the smallest values of r/a, up to 0·20, the formula of Schröedinger† was used. For this value of r/a both methods gave the same result for X/r, but, as would be expected, this formula no longer holds, as r/a increases.

TABLE 80

Minimum Value of X/r for Values of r/a from 0 to 1·50

r/a	0·00	0·01	0·02	0·03	0·04	0·05	0·06	0·07	0·08	0·09
0·0	1·0000	0·9999	0·9997	0·9994	0·9990	0·9984	0·9977	0·9968	0·9958	0·9946
0·1	0·9934	9920	9905	9888	9870	9851	9831	9809	9786	9762
0·2	9737	9710	9682	9653	9623	9592	9560	9527	9492	9456
0·3	9419	9382	9344	9305	9265	9224	9182	9138	9093	9047
0·4	9000	8952	8903	8853	8802	8750	8698	8645	8592	8538
0·5	8484	8429	8374	8319	8263	8207	8151	8094	8037	7979
0·6	7920	7860	7800	7739	7678	7616	7554	7493	7432	7372
0·7	7312	7252	7192	7132	7072	7012	6953	6894	6835	6776
0·8	6718	6660	6603	6547	6492	6438	6385	6333	6281	6230
0·9	6179	6129	6079	6030	5981	5933	5885	5838	5792	5747
1·0	5703	5659	5616	5573	5531	5489	5448	5408	5368	5329
1·1	5290	5251	5213	5176	5139	5103	5067	5032	4997	4962
1·2	4928	4895	4862	4829	4797	4765	4733	4702	4671	4641
1·3	4611	4582	4553	4524	4496	4468	4440	4413	4386	4359
1·4	4333	4307	4281	4256	4231	4206	4181	4157	4133	4109
1·5	4085									

By the aid of table 80 the surface tension can be calculated accurately from the pressures required to liberate bubbles from two tubes of different radii which are immersed to the same depth below the surface of the liquid. Let r_1, r_2 be the radii of the tubes, h_1, h_2 the pressures, measured in cm. of the liquid concerned, which are required to liberate bubbles, and t the depth to which each tube is immersed. Then from (8)

$$h_1 = \frac{a^2}{X_1} + t, \; h_2 = \frac{a^2}{X_2} + t$$

* Compare Ferguson, *Phil. Mag.*, 1914 [6], **28**, 128; Schroedinger, *Ann. Physik*, 1915, **46**, 413.

† $a^2 = hr\left(1 - \frac{2}{3}\frac{r}{h} - \frac{1}{6}\frac{r^2}{h^2}\right)$

Therefore

$$H = h_1 - h_2 = a^2(1/X_1 - 1/X_2)$$

or

$$a^2 = \frac{H}{1/X_1 - 1/X_2} \quad \ldots\ldots\ldots\ldots\ldots\ldots (10)$$

The use of this equation and the table are best explained by means of an example. With the apparatus described on page 208, the following values were found for benzene at 20°: $r_1 = 0{\cdot}007525$ cm., $r_2 = 0{\cdot}0600$ cm., $H = 6{\cdot}81$ cm. of water at 15° = 7·755 cm. of benzene at 20°.

As a first approximation, take $X_1 = r_1$, $X_2 = r_2$.

Then

$$a^2 = \frac{7{\cdot}755}{116{\cdot}2} = 6{\cdot}675 \text{ sq. mm.}$$

Using this value of a^2 to calculate r_1/a and r_2/a, it is found that

$$r_1/a = 0{\cdot}029 \qquad r_2/a = 0{\cdot}232$$

From table 80 the corresponding values of X/r are

$$X_1/r = 0{\cdot}9994 \qquad X_2/r = 0{\cdot}9649$$

whence

$$X_1 = 0{\cdot}007522 \qquad X_2 = 0{\cdot}0579$$

Putting these values in (7), $a^2 = 6{\cdot}703$ sq. mm.

A further application of this method of successive approximations gives the same result for a^2.

At 20°, for benzene, $D - d = 0{\cdot}8771$, $g = 981$ cm./sec.^{2}, from which $\gamma = 28{\cdot}84$ dynes/cm.

This method of calculation is accurate for any size of tube giving values of r/a covered by table 80. It is, however, very tedious when a large number of results have to be dealt with, and a much simpler method can be used if the values of r_1 and r_2 fall within certain limits. In practice tubes of radii less than 0·005 cm. are difficult to use, since they are readily blocked by dust particles; on the other hand, tubes of radii greater than 0·010 cm. give pressures which are small and cannot be measured accurately. The radius of the wide tube is conveniently fixed at between 0·100 and 0·200 cm. For tubes of these radii and liquids with values of a^2 greater than 3 mm.^{2} it is found that the surface tension may be calculated by the simple empirical formula*

$$\gamma = AP\left(1 + 0{\cdot}69r_2\frac{gd}{P}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots (11)$$

* Sugden, *J.C.S.*, 1924, **125**, 29.

Here A is a constant for the apparatus which is determined chiefly by the radius of the smaller tube, and P is the difference in pressure required to liberate bubbles from the two tubes, and is expressed in dyn./cm.^{2}. This simple expression, when tested by comparison with the more accurate method, using equation (11) and table 80, is found to be accurate to one part in 1000 within the limits stated above. It is, therefore, amply accurate, since the errors of observations are usually considerably larger (about 1 in 200).

INDEX

(Names of authors are indicated by italics.)

Acids 167
Alcohols 167
Aluminium Compounds 147
Anomalies in Simple Molecules 170
Antimony 188
Arsenic Compounds 188
Associated Liquids 157ff
Atomic Parachors 38, 181
——, and Atomic Number 182
Atoms, Electronic Structure of 74ff
Azimuthal Quantum Numbers 66
Azoimides 123
Azoxy-compounds 119

Balmer's Series 55
Barium 187
Bashforth and Adams 12, 214
Bell and Bennett 122
Benzil 47
Beryllium Compounds 145
β-Diketones 149
Biltz and Klemm 95
Bohr 60ff
Boron Compounds 187
Bosanquet 214
Bubble Pressure 10, 217
Burrau 193

Cadmium 187
Calcium 187
Capillary Rise 9, 205
Carbonic Esters 117
Chapman 1
Chelated Compounds 142ff
Chromyl Chloride 125
Cohesion 4, 16ff
Contact Angle 6
Co-ordination Compounds 138ff
Copper 186
Covalency 89ff, 110

Debye 88, 99ff, 178
Density, Determination of 203
Dielectric Constants 98ff
Dipole Moments 105, 107
Dirac 193
Drop Weights 11ff
Duplet Linkage 91
Dupré 16

Edser 16, 21
Electrovalency 87, 110
Eotvos 28
Esters 42

Fajans 95
Ferguson 23

Gallium 187
Gold 186
Goldhammer 27

Harkins and Brown 13
Heisenberg 193
Heitler and London 195
Hicks 57
Higher Halides 128ff
Higher Valencies 114ff
Hildebrand 17, 162
Hund's Theory of Spectra 69ff

Inert Gases 186
Ingold and Shoppee 48
Inner Quantum Number 73
Iredale 15
Isostere 94

Jaeger 180

Kossel 86

Langmuir 87, 93, 128
Laplace 7, 19, 20, 213
Lewis 79, 86, 90ff
Lindemann and Thiele 124
London 195, 196
Lowry 108, 114, 115, 143

McBain 164
Macleod 26
Magnetic Quantum Numbers 69
Main Smith 71, 91
Mercury Compounds 111, 187

Metals 172ff
Mills and Gotts 143
Molybdenum 189
Morgan 142
Moseley 54
Multiplicity of Spectral Lines 59, 71
——, and Atomic Number 72
Mumford and Phillips 51

Nickel Carbonyl 189
Nitrites 118
Nitro-compounds 119
Nitroso-compounds 118
Normal Valency 92

Octet Rule 79, 86, 90, 120, 125, 129, 199
Optical Activity and Semipolar Double Bonds 121

Parachor, Additive Properties of 33ff, 41
—— and Association 165
—— and Critical Volumes 31
—— and Electron Sharing 110
—— and Molecular Dimensions 32
—— and Molecular Refraction 40
—— and Singlet Linkages 131ff
—— and Unsaturation 40, 112
——, Atomic Constants 38, 181
——, Structural Constants 40
Paraldehyde 45
Pauli's Exclusion Principle 70
Philip 124
Phillips 121
Phorone 49
Phosphorus Compounds 116, 188
Phthalyl Chloride 47
Polar Bonds 86
Prideaux 129

Quantum Numbers 63, 66, 69, 70
Quantum Theory and Atomic Structure 60ff
Quantum Theory of Valency 191
Quinones 45

Ramsay and Shields 10, 23, 28, 157
Refractivity 40
Rutherford 53
Rydberg's Constant 57

Salts 175ff
Schroedinger 109, 191, 219
Selenium Compounds 126
Semipolar Double Bonds 114ff
Series Spectra 55ff
Shared Electrons 90, 107, 193ff
Sidgwick 115, 129, 139, 140
Silicon 187
Silver 186
Singlet Linkages 129ff
Spin Quantum Number 71, 196
Stoner 71
Succinyl Chloride 47
Sulphonal 172
Sulphonium Mercuri-iodides 153
Sulphur Compounds 166, 188
Surface Tension, Definition of 6
——, Measurement of 8, 205
——, Variation with Temperature 23

Thallium Compounds 145
Tin Compounds 150, 187
Titanium 187
Total Surface Energy 29
Transition Elements 78
Trouton's Rule 161
Tungsten 189
Turner 164

Valency, Polar 86
——, Non-polar 89
——, Normal 92
——, Higher 114ff
van der Waals 4, 23
Verschaffelt 27
Viscosity of Gases 1

Walden 159, 160, 177
Wave-Mechanics 191
Worthington 15

Zeeman Effect 73
Zinc 187